Maria Carolina Salis Gomes

Licenciada em Conservação e Restauro

Investigating surface treatments and coatings, their history, application and detection on selected pigments: Lead White, Zinc White and Titanium White

Dissertação para obtenção do Grau de Mestre em
Conservação e Restauro

Orientador:
Professora Doutora Leslie Carlyle
Professora Associada
Faculdade de Ciências da Universidade NOVA de Lisboa

Co-orientador:
Professor Doutor Klaas Jan van den Berg
Conservador Sénior
The Cultural Heritage Agency of the Netherlands

Júri:
Presidente: Prof. Doutora Maria João Melo
Arguente: Prof. Doutora Joana Lia Ferreira
Vogal: Prof. Doutora Leslie Carlyle

FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Setembro 2018

Maria Carolina Salis Gomes

Department of Conservation and Restoration
Master degree in Conservation and Restoration

Investigating surface treatments and coatings, their history, application and detection on selected pigments: Lead White, Zinc White and Titanium White

Dissertation presented at Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, in fulfilment of the requirements for the Master degree in Conservation and Restoration, specialisation in Conservation Science

Supervisors: Leslie Carlyle
Klaas Jan van den Berg

September 2018

Investigating surface treatments and coatings, their history, application and detection on selected pigments: Lead White, Zinc White and Titanium White

Acknowledgments

The investigation for this thesis was carried out at the Cultural Heritage Agency of the Netherlands (RCE) within the scope of the 2015-2018 project, “Cleaning of Modern Oils Paints” (CMOP), a European funded program with the primary objective of improving our understanding of the composition of modern artists oil paints. This project was made possible by Professors Leslie Carlyle and Klaas Jan van den Berg who proposed the subject of pigment surface treatments and to whom I am deeply grateful for introducing me to a truly fascinating subject, sharing their deep knowledge and experience, for their availability, fruitful discussions, and also for their guidance and support.

I am indebted to Inez van der Werf, for her invaluable support and availability to discuss the different issues at stake in the research.

My deep appreciation to Birgit van Driel for providing sample material and for all her help, valuable suggestions and friendship; Henk van Keulen for all his support and instruction with the mass spectrometry techniques; Ineke Joosten for all the beautiful FEG-SEM images; Nel for enabling my stay in Amsterdam; Matthijs de Keijzer for his help with patent research; and all the people who found the time to discuss various topics arising from the research.

I would also like to thank the following people: Coos van Waas and Daphne van Mansom from Royal Talens© for sharing their experience and thoughts on this subject; Brenda Rossenaar and Arne Jansen from AKZO NOBEL Specialty Chemicals © for providing the (S)TEM-EDX results and fruitful discussion; Conny te Walvaart and Tanja Takman from BASF© for their availability to discuss this commercially sensitive subject.

My thanks to the Conservation Department of FTC-UNL, for the learning experience during these past years. It was truly wonderful. I would also like to thank RCE for providing the technological means to carry out the research and for enabling access to all the expertise of such a high level group of researchers.

To Cátia Ferreira, my fellow colleague in this investigation, thank you for sharing this intensive and magical journey of discovery and learning with me.

Finally, my thanks to new and old friends and colleagues, both in Lisbon and Amsterdam who accompanied me in this journey and provided invaluable support.

Abstract

The present work looks at pigment surface treatments and is divided in two parts. Part I explores the relationships between pigment manufacturers, raw materials suppliers, and the artist's oil paint manufacturer, and describes surface treatments and coatings. This is followed by a summary of the history and characterization of surface treatments and introduces the role of pigments in the formation of certain paint defects in relation to these surface treatments. Finally, it presents a tentative identification of the surface treatments of the white pigments selected for study. The research in Part I involved collecting information through research into the patent and technical literature in conjunction with interviewing a global manufacturer and supplier of raw materials/pigments and an artist's oil paint manufacturer. This exploration revealed that pigment surface treatments can be very complex consisting of either an inorganic or organic component or both, applied in very small amounts (up to 10% wt of the pigment). This work revealed that surface treatments may find their origins very early on, as in the 14th century Montpellier Manuscript, and that treatments re-emerge in response to industrial uses and needs not specifically linked to artist's oil paint manufacturers. Materials such as waxes and stearates, known additives for oil paints, but also alkyds, developed as organic binders, were found to have been used as surface treatments for pigments.

Part II focuses on the detection and identification of surface treatments on the selected pigments, Lead White, Zinc White and Titanium White, and describes the multi-analytical approach used to investigate their surface treatments with electron microscope techniques (SEM-EDX, FEG-SEM and (S)TEM-EDX) and hyphenated mass spectrometry techniques (EGA-MS, Py-GC//MS and Py-THM-GC/MS, and DTMS). This study highlights the importance of gathering information on the pigment's provenance and material characterization and reflects on the implications of terminology and commercial secrecy for surface treatment detection and identification. Regarding the detection and identification of inorganic treatments, both FEG-SEM and (S)TEM-EDX proved to be effective for this purpose. These techniques also provided evidence which shed light on the method of manufacture of the pigments. Although the analysis of the organic fraction present in the pigment samples proved to be challenging, pyrolysis methods did enable the identification of anticipated materials (as was the case of the polyols in Titanium White pigments) as well as the discovery of unexpected compounds such as anti-oxidants.

Keywords: Surface treatment; Titanium White; Lead White; Zinc White; Pigment

Resumo

O presente trabalho analisa tratamentos de superfície de pigmentos e encontra-se dividido em duas partes. A Parte I explora as relações entre os fabricantes de pigmentos, os seus fornecedores e os fabricantes de tinta a óleo para artista e procura definir os tratamentos e revestimentos de superfície. De seguida apresenta-se uma breve história e caracterização dos tratamentos de superfície e introduz-se o papel dos pigmentos tratados na formação de certos defeitos em tintas. Finalmente, apresenta-se uma tentativa de identificação dos tratamentos de superfície dos pigmentos brancos escolhidos para estudo. Esta pesquisa envolveu a recolha de informação por meio de pesquisa de patentes e literatura técnica, em conjunto com entrevistas efetuadas a um fabricante e fornecedor global de matérias-primas/pigmentos e a um fabricante de tintas a óleo para artista. Esta exploração revelou que os tratamentos de superfície de pigmentos podem ser muito complexos consistindo de um componente inorgânico, orgânico ou ambos, aplicados em quantidades diminutas (até 10% do peso do pigmento). Este trabalho revelou que os tratamentos de superfície podem encontrar suas origens muito cedo, evidenciado no Manuscrito de Montpellier do século XIV, e que os tratamentos reemergem em resposta a usos industriais e não a necessidades especificamente ligadas aos fabricantes de tinta a óleo para artista. Materiais como ceras e estearatos, conhecidos aditivos para tintas a óleo, mas também materiais alquídicos, desenvolvidos como ligantes, terão sido usados como tratamentos de superfície para pigmentos.

A Parte II foca-se na deteção e identificação de tratamentos de superfície nos pigmentos selecionados, Branco de chumbo, Branco de zinco e Branco de titânio, e descreve a abordagem multi-analítica usada na sua investigação, recorrendo a técnicas de microscopia eletrónica (SEM-EDX, FEG-SEM e (S)TEM-EDX) e técnicas de espectrometria de massa (EGA-MS, Py-GC/ MS e Py-THM-GC/MS, e DTMS). Este estudo destaca a importância de recolher informação sobre a proveniência e caracterização material do pigmento e reflete sobre as implicações da terminologia, e do sigilo do tratamento, na deteção e identificação de tratamentos de superfície. Relativamente à deteção e identificação dos tratamentos inorgânicos, tanto o FEG-SEM quanto o (S)TEM-EDX mostraram-se eficazes para esse fim. Estas técnicas forneceram também dados para esclarecer o método de fabricação dos pigmentos. Embora a análise da fração orgânica presente nas amostras de pigmento se tenha mostrado um desafio, os métodos de pirólise possibilitaram a identificação de materiais antecipados (como foi o caso dos polióis em pigmentos de Branco de Titânio), bem como a descoberta de compostos inesperados como anti -oxidantes.

Palavras-chave: Tratamento de superfície; Branco de Titânio; Branco de Chumbo; Branco de Zinco; Pigmento

Index of Figures

Index of Tables

Index of Figures in Appendix

A	Anatate form of Titanium White
DTMS	Direct Temperature Mass Spectrometry
EGA-MS	Evolved Gas Analysis Mass Spectrometry
CMOP	Cleaning of Modern Oils Paints Project
FEG-SEM	Field Emission Gun Scanning Electron Microscope
R	Rutile form of Titanium White
RCE	Cultural Heritage Agency of the Netherlands
SEM-EDX	Scanning Electron Microscope - Energy Dispersive X-ray
(S)TEM-EDX	Scanning Transmission Electron Microscope - Energy Dispersive Spectroscopy
TIT	Total Ion Thermogram
TMP	Trimethylolpropane
UTD	Ultra-Thermal Desorption
Py-GC/MS	Pyrolysis Gas Chromatography/ Mass Spectrometry
Py-THM-GC/MS	Pyrolysis Gas Chromatography with thermally-assisted hydrolysis and methylation Mass Spectrometry
LV	Low Vacuum
BF	Bright Field

1. Introduction

Background on pigment manufacture

As fine art materials represent a relatively small market, few pigments are specifically developed for this market. By the middle of the 19th century and throughout the 20th and 21st century, new colours for artists are adopted from industrial chemical processes and directed to wide markets such as the textile and the printing industries [1,p.11; 2; 3]. Furthermore, as pigment use diversified so did the refinement of its manufacture. Modern industrially produced pigments can be supplied with surface treatments that, in spite of having similar chemical compositions, can present different surface characteristics. These modifications aim to improve the performance of pigments in different media and thus enable producers to provide a broader range of pigment grades suitable for the different requirements of each market (e.g. architectural coatings, automobile paints, plastics, and cosmetics) [4, p. 3]. However, pigment surface treatments and coatings are industry-kept secrets and therefore remain confidential [5, p. 29]. For conservators, the presence and composition of these treatments is of concern since detailed knowledge of the materials used in modern oil paints is necessary in order to understand degradation phenomena and for research calling for paint modelling using highly characterized historical reconstructions [6, 7].

Thesis outline

The investigation for this thesis was carried out at the Cultural Heritage Agency of the Netherlands (RCE) within the scope of the 2015-2018 project, "Cleaning of Modern Oils Paints" (CMOP), a European funded program with the primary objective of improving our understanding of the composition of modern artists oil paints [8].

The focus for this thesis is on important 20th century white pigments: Lead white, Zinc white and Titanium White. In addition to their unique historical importance and their popularity among modern artists, Lead white and Zinc white have been implicated in paint degradation primarily due to their reactivity in oil media [9; 10] whereas Titanium White can exhibit surface powdering (chalking) due to its photocatalytic activity, as more recently discussed by van Driel (2018) [11].

This investigation into pigment coating is divided into two parts. Part I covers an extensive literature and begins with a brief exploration of the relationships between pigment manufacturers, their suppliers, and the artist's oil paint manufacturer. Key literature sources identified were Barnett (1949) [12], Fisher (1950)[13], Merkle and Schafer (1973) [14], Hays (1984) [15], Schroder (1988) [4], and Bugnon (1996) [16]]. These invaluable sources provide us insight on the history and modern developments on surface treatments. Information was also found by researching patent, and pigment and paint technical literature in conjunction with interviewing a global manufacturer and supplier of raw materials/pigments and an artist's oil paint manufacturer. Next the definition of surface treatments and coatings and the history of surface treatments and their characterization is presented. Following is an exploration of the role of pigments in the formation of certain paint defects in relation to these surface treatments. Finally, surface treatments of the white pigments chosen for study are identified. This step is fundamental in order to have references regarding treatments and materials and thus be able to identify substances as surface treatments. As will be seen this is particularly relevant when investigating the organic component.

In Part II a combined analytical approach that aimed to enable the investigation of both the organic component and the inorganic component of surface treatments on unbound pigments using electron microscope and hyphenated mass spectrometry techniques is described. In a first approach, Scanning Electron Microscope Energy Dispersive X-ray (SEM-EDX) was carried out as a first screening of samples. Although Secondary Electron (SE) in high vacuum is commonly used to investigate pigment morphology in this case, in order to avoid charging of the pigment samples, imaging was carried out in Backscaterring Secondary electrons (BSE) with Low Vacuum (LV) [20]. Energy Dispersive x-ray spectroscopy (EDX) provides

an overall idea of the elemental [17]. Field Emission Gun Scanning Electron Microscope (FEG-SEM) was used for a selection of pigment samples. This technique offers higher- resolution than SEM-EDX and enables the visualization of particle topography [18]. The analytical technique, (S)TEM-EDX allows for an investigation of the individual pigment particles, and can indicate whether an inorganic coating is present [11, p. 117; 19, 20].

The investigation of the organic component, as van Driel (2018) notes "is less straightforward" [11, p.117] especially when investigating pigments where there is little information, or no information at all on their provenance. In a first approach Evolved Gas Analysis Mass Spectrometry (EGA-MS) was carried out as a first screening of the pigment samples. This technique is a form of direct pyrolysis which analyzes the gas emitted while the sample undergoes decomposition or desorption and the resulting thermogram is analysed using a combination of extracted ion chromatograms and average mass spectra is obtained [21]. Py-GC/MS is also proposed as a suitable method for the analysis of the organic component [11, p. 278, 20]. In some samples, Pyrolysis coupled to gas chromatography – mass spectrometry (Py-GC/MS), with thermally-assisted hydrolysis and methylation (THM-GC/MS), was performed. The method applied was Ultra Thermal Desorption (UTD) method, meaning the samples were investigated through "slow pyrolysis" and not as flash pyrolysis. This method, developed at RCE, involves a temperature program that enables a one-shot analysis with evaporation before pyrolysis. Finally, Direct Temperature Mass Spectrometry (DTMS) was used for three Titanium White pigments. DTMS results were not conclusive and require further investigation which is beyond the scope of this thesis. The diagram below (see fig.1) illustrates the approach that has been described.

For this investigation dry pigment samples were collected with differing degrees of information on their provenance. Pigments were collected from the RCE Reference Pigment Collection, from which little was known aside from the date of incorporation and/or the source. Two Lead White pigments from the Carlyle MOLART Fellowship[22] which had been previously been characterized with SEM-EDX were selected for study and the Titanium White pigments were selected from pigments researched by Birgit van Driel in her PhD [11]. In this thesis the investigation of the Titanium White samples focuses on the organic component of the treatment. As will be seen, the use of pyrolysis techniques enabled the confirmation of the presence of a polyol and the confirmation of the presence of new compounds.

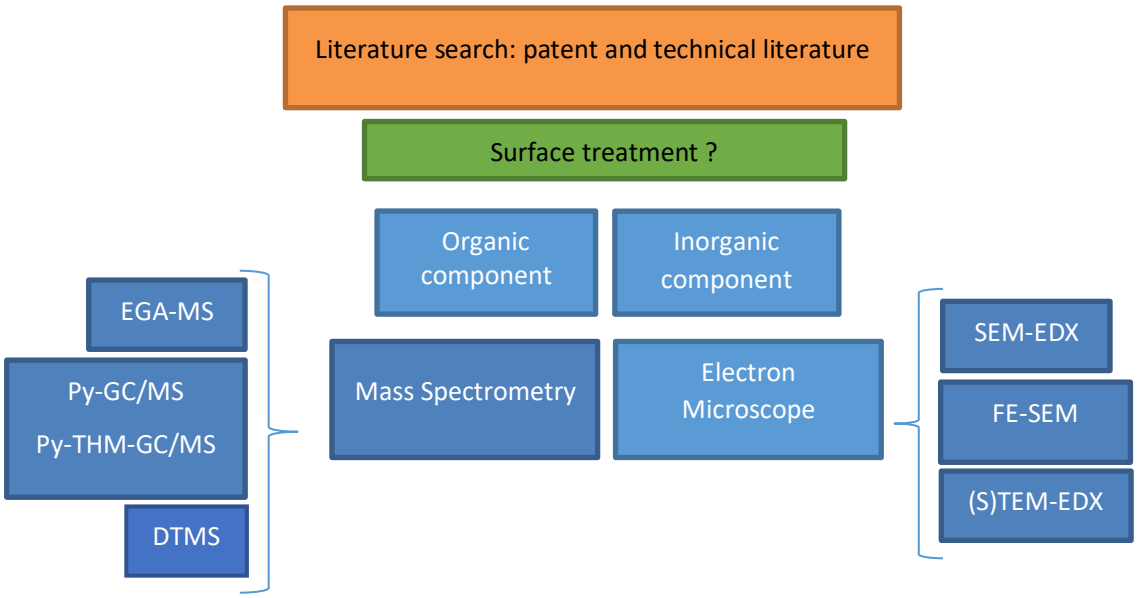


Figure 1. Diagram illustrating the approach for the investigation of surface treatments

1.1 Modern pigments: challenges for paint manufacturers and for conservators

As noted above, pigments used in oil paint manufacture are produced for large industries with their own requirements and commercial concerns. Mark Golden, who developed the highly successful company, Golden Acrylic Paints for artists wrote an article in 2016, "Manufacturing paints: Keeping pace with change" [23] where he notes that, while it is good that there are other users such as the automotive industry which share requirements with artist paints, such as lightfastness and high quality paint, and thus function as a driver for quality, it is a problem that artist's paint manufacturers have little control regarding their raw materials. Indeed, as Golden notes, when considering all the raw materials used, it is the pigments that are the most subject to change.

For artists' oil paint manufacturers maintaining confidence in their product is of utmost importance and, therefore, raw material availability and the need to change paint formulations are carefully considered. As Mark Golden (2016) points outs, paint manufacturers need to achieve greater permanency, adapt to regulatory changes and market forces. This may lead to shifts in formulations and pigment choices [23].

A key issue which became evident in this research is that changes in production, such as the creation of a different particle size range or an alteration in surface treatment, may occur without the pigment manufacturer necessarily informing the paint manufacturer. This lack of transparency was explained by two representatives from the BASF© company Conny te Walvaart, Account manager for pigments and coatings, and Tanja Takman, Account manager for coatings, in an interview on February 6, 2018 carried out by this author[1] . They stated that because pigment surface treatments are part of what makes the pigment competitive within the market, this information is proprietary. As a result, any information disclosed, either in patents or in the technical literature is deliberately vague to avoid imitation by the competition.

Another issue for paint manufacturers is the correct selection of the pigment grade. Manufacturers aim to produce a high-quality and economical paint and the pigment represents the single largest cost component [25]. Pigment selection is a compromise between different requirements: color and opacity, insolubility, lightfastness, weatherability, chemical resistance, and economic constraints [22]. Manufacturers such as BASF© offer large pigment portfolios[2], and pigment data-sheets will show pigments that are multifunctional since they are listed as appropriate for use both in plastics, paints or textiles. Therefore, pigments can be treated with substances that although compatible with some vehicles may not respect all requirements. As Levison (1973) points out, although there can be similarities between artists' and industrial paints, the requirements for stability, lightfastness and the pigment's contribution to paint durability are different [26].

In an interview with Coos van Waas, chemical engineer and product specialist R&D, and Daphne van Mansom, laboratory manager, October 11, 2017, at Royal Talens©, an artist's materials manufacturer and supplier, they explained that with regard to their artist's oil paint, prior to purchase, they carry out rigorous testing for all their raw materials (all properties are tested at 40°C during six months), and like Mark Golden, they highlighted the importance of product availability. These representatives emphasized that they rely on having a good relationship with their supplier.

For conservators, conservation scientists and technical art historians who wish to understand the composition of a given oil paint, the fast pace of change within the paint and coatings industry is an additional challenge since the composition of any particular paint is like a snapshot in time and thus not necessarily representative.

---

[1] The research on pigment surface treatments and coatings was carried at RCE in conjunction with Cátia Ferreira, Conservation and Restoration Masters student [24] from the NOVA University of Lisbon, in the context of a master thesis curricular internship. This interview was conducted by Cátia Ferreira, the author and Klaas Jan van den Berg (masters project supervisor) in Appeldorn at Royal Talens© headquarters.

[2] As of December 16, 2017, on the BASF© website is the section "Markets & Industries" which directs the consumer to their areas of interest and each area subdivides into other markets. For instances, in Paints and Coatings there is Architectural coatings, Industrial Coatings, Automotive Transportation, and Furniture & Flooring.

1.2 Pigment surface treatments and coatings

Pigment surface treatments, as Schröder (1988) explains, consists of the "modification of the surface character of a pigment in a desired manner where the original pigment surface can either be modified or replaced by a completely new surface" [4, p.3]. Some of the major objectives of these treatments include, better particle dispersion, improved mechanical properties, and improved effectiveness in light scattering in a paint film [4, 19].

A **surface treatment**, or **surface-modification,** can be understood as an umbrella term for various methods of treatment application and technological processes that involve the action of chemical and/or physical agents to alter surface character and improve pigment properties [27]. These modifications, depending on the pigments' nature (organic or inorganic), manufacturing route and intended use, can occur during the synthesis of the particle (in-synthesis) and/or afterwards, in a post-synthesis phase after pigment particles are fully formed [4, 5, 28].

It is important to note that although **surface treatment and coating** are terms often used interchangeably, a surface treatment does not always imply a coating treatment . By definition, a **coating** involves the deposition of other matter, as a thin layer, onto the surface of the pigment particles [29]. This can occur during synthesis but also after synthesis in a post-production phase. Coating can refer to the act of coating (as a verb), to designate the agent (the adjective) relating to a step in the manufacture process, or it can refer to the technology or even to all of the above. For the investigation of surface treatments and coatings it is very important to understand that different contexts may imply different treatments. Another popular term is encapsulation or microencapsulation. This refers to surface treatments which are polymeric in nature (e.g. [16, 19, 27] for more detailed information on this subject) and, as was discussed in the meeting with BASF, this term is used to refer to the total coverage of the pigment.

The earliest written source, to date, where a pigment treatment is described is in The Montpellier Manuscript which dates from the 14th century and calls for the use of natural materials such as egg on Azure and fish glue on Cinnabar[3] [30]. Regarding more modern times, records were found dating to the late 19th century describing the use of "adhesive substances" soluble in water [31] describing the use of materials such as waxes [32] and metallic stearates [33, 34] applied in small amounts during pigment manufacturing as can be seen in Appendix I (see fig. 1, 2 and 3). O'Brien in his patent dated from 1937 proposed the use of fatty acids and explains, the purpose of these additions is to "be clearly distinguished from the mere addition of stearic and oleic acids and certain salts of these acids to paints for the purpose of preventing settling and giving body to the paint. My process is designed for a different purpose; namely, the **alteration of the properties of the pigment itself** which is **brought about preliminary to the grinding of the pigment in oil**. Furthermore, where heretofore the oleic and stearic acids and their salts have been added to paints, from 1 to 2% of the total weight of the paint including the vehicle is necessary to accomplish the desired effect in the paint. By my process of treating the pigments **a very much smaller quantity** of oleic and stearic acids will produce the totally different effect in the pigment-itself, for usually with oleic or stearic acid equal to 0.1% of the weight of the dry pigment I am able to cover the pigment with the requisite amount of protective colloid or deflocculating agent to yield a pigment possessing the new modified properties" [35, p. 1].

These finding show us that surface treatments on pigments are not modern additions, but further investigation needs to be conducted in order to better understand how materials and methods of application evolved and to correlate this to the different industrial requirements and pigment markets. Also, it is important to highlight that both waxes and metallic stearates are known additives applied by the oil paint manufacturers to correct or improve paint formulations [36].

Bugnon (1996) provides background for the evolution of the surface treatment and highlights key motives that lead to the surface treatment of both organic and inorganic pigments: "historically, the preparation of inorganic pigments pushed the pigment producer to use spacers, anti-sintering, agents or

[3] The reference was provided by Dr. Mark Clark in personal correspondence March 27, 2017.

growth inhibitor compounds. Further, the stability of the inorganic pigments against light, heat or chemical aggressions, was strongly improved by deposition of metal oxides on their surface. With the larger use of organic pigments the treatments were carried out by the end-user, mostly paint manufacturers, with the purpose to improve in most cases the dispersibility, the dispersion stability and the rheology of the paint. The surface treatment of organic pigments started in ink applications with very fine and very transparent pigments where the inhibition of crystal growth plays a major role during their production and the dispersibility has to be good in the application" [16, p. 39].

1.2.1. Two approaches for surface treatments: during-synthesis and post-synthesis

In the literature [4, 27] it was found that there are two main occasions where pigment manufacturers apply surface treatments. The following explanation highlights key steps and materials applied.

During synthesis

The first approach involves the tailoring of pigment surface properties during particle synthesis. At this stage pigments which are formed through direct precipitation can be treated with **surfactants**, low weight molecular compounds, generally containing two groups of opposite polarity and solubility: a hydrophilic group, a "head", which may be polar or non-polar and a lipophilic group, a "tail", generally consisting of aliphatic or hydrocarbon residues (see below fig. 2) [37].

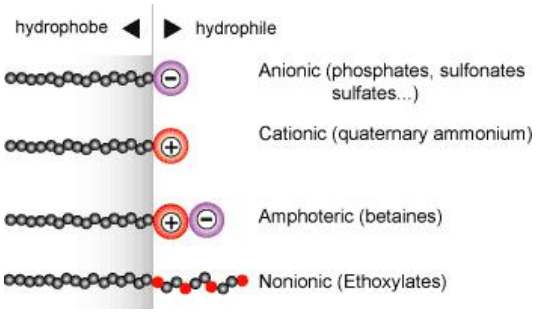


Figure 2. Surfactants depending on their charge and charge distribution, can be divided into ionic (cationic or anionic), amphoteric and nonionic (http://www.uniqchem.com/dispersing-technology/?lang=de)

These substances form micelle-like structures and enable the producer to **control the particle size and shape** (e.g. azo pigments, iron oxides) [4].

Also, molecules or ions of many inorganic and organic pigments such as Copper Phthalocyanine Blue and Titanium White, are polymorphic, and can form different arrangements in the crystal lattice resulting in different crystal phases/modifications [38, p. 14]. These forms have different physical properties and can be unstable. Therefore manufacturers **influence crystal phase/modification** by the addition of substances that absorb[4] selectively on different crystal faces inhibiting crystal growth [4]. Known examples of such materials are rosin and Turkey red oil[5] [4, p. 4].

Also, inorganic pigments that go through a calcination stage can be treated prior to calcination to **avoid sintering[6] and loss of shape** with anti-sintering layers formed by substances such as poly(phosphates), silica, alumina and oxide hydroxides [4, p. 4].

Pigments such as Copper phthalocyanine blue can be synthesized/precipitated simultaneously with substances that act as surface treatments in a process known as **pigment resination** [3, 4]. This treatment is reported to be one of the oldest forms of treatments and has multiple effects. Pigment particles are enveloped in resin thus decreasing particle to particle contact; this enveloping leads to a looser powder

[4] According to Lu (2009), "absorption is the incorporation of an aqueous chemical species into a solid phase by diffusion or some other means such as dissolution of the solid followed be re-precipitation of the solid" [39, p. 99].

[5] As of 22 of September, 2018, Cameo website describes Turkey red oil as a "viscous liquid used as an anionic surfactant prepared by treating castor oil with sulfuric acid followed by washing and neutralization. This oil was used as a dyeing assistant in the 19th century, also called "alizarin assistant", was used in soaps and in the manufacture of leather and paper".

[6] According to the website Britannica, as of 22 September, sintering is defined as "the welding together of small particles of metal by applying heat below the melting point"

compactation and the obtaining of a softer texture that results in an easier dispersion of pigment particles. Also, because rosin is a crystal growth inhibitor, crystal sizes are smaller[7] (see below fig. 3) [4, 5; 14, p. 159].

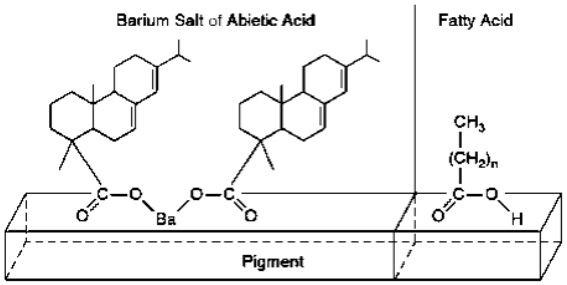


Figure 3. Treatment of pigment surface with rosin and fatty acids. (Illustration from Vernadakis 2007, p. 11 [40])

Post-synthesis

After pigment particles are fully formed their surface character can be further modified. Treatments applied at this stage are commonly designated as *coating*, *aftertreatment* [41, 42, 43], *finishing* [27, 44], and *postconditioning* [5].

Pigment coating is ideally, colourless or with no strong influence on the colour and acts as a "barrier" that establishes a physical and chemical boundary between the pigment and binder. The coating interrupts interactions by adjusting the character and energy of the pigment surface between the pigment and binder and improves the weathering properties of the pigments in the binder system (i.e. stability against UV, humidity, etc.). The coating creates an affinity with the binder that improves application properties (e.g. pre-wetting of particle, dispersion behavior, settling and prevent of *flocculation* (see text 1.3.2) [42, p. 5]. The coating itself results from the interaction of the pigment particle surface with "molecules that can be tailor-made through chemical modifications so that they have a higher affinity for selected interfaces, such as solid/liquid and coating/liquid" [45, p. 70].

The coating can be described as a thin layer that is better observed at a nano-scale [16]. The structure of the coating and the composition of the treated pigment particle can vary. It may consist of a monomolecular layer or a multilayer and it may contain one or several substances. It can consist of inorganic (e.g. Silica Oxide (SiO_2), Alumina Oxide (Al_2O_3), Zirconium Oxide (ZrO_2)), organic (e.g. polyalcohols, siloxanes, organo-functional silanes or titanates) or combined inorganic/organic compounds [42, p. 5]. The coating can vary in thickness, porosity and density [14, p. 157; 42, p. 67; 38]; and it can be partial or total depending on the type of pigment and the nature of the application method [4,p. 36]. As can be seen below (fig. 4), in practice different coating possibilities can occur.

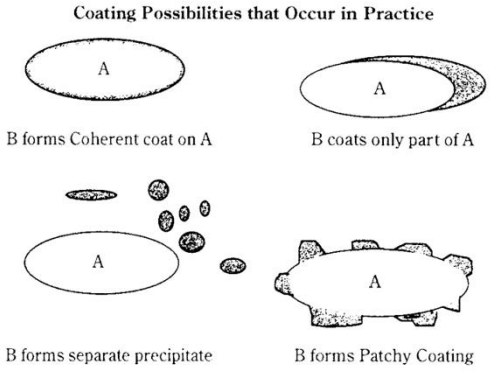


Figure 4. Different coating possibilities that can occur in practice (Illustration from Egerton 1998, p. 53 [19])

[7] According to Merkle and Schäfer (1988) note that natural rosin, abietic acid, is sensitive to oxidation which has an unfavorable effect on storage stability. Furthermore, due to its low melting point the mechanical properties of the paint film are also affected [14].

The coating treatment is often applied with pigment particles suspended in water or in an aqueous solution with the agents/substances deposited by precipitation followed by adsorption or steam hydrolysis [42].The characteristics of the coatings, the substances used, and the method of application, are carefully controlled by the manufacturer and are chosen according the nature of the pigment and its end use. As explained by Vernovski and Verhovsek (2014), in the case of the TiO_2 pigments, "the base pigment is affected by the manufacturing process, the crystal structure, and particle size distribution. The additives during manufacture and the morphology of the treatment layers will affect the final properties of the pigment" [46].

A popular treatment involves variations on the conditions of silica and alumina precipitation. As explained by Veronvski and Verhovske (2014), at an acidic or neutral pH, silica is deposited as submicroscopic particle joined together in a gel-like structure, termed "fluffy" silica. This material acts as a spacer, improves optical efficiency and increases oil absorption. At a basic pH, dense silica can be deposited forming a shell which does not increase the oil absorption. The combination of a coating of "fluffy" silica with "fluffy" alumina (precipitation of hydrous alumina) finds use in High PVC Paint and matte dry-hiding formulations [46]. Also, according to Vernadakis (2007), an alumina coating can increase the functionality of the particle surface by creating active adsorption[8] sites for the resin molecules [40, p.16]. Furthermore, as Winckler (2003) notes, precipitation can be performed in a batch or in sequence, and materials can be simultaneously precipitated as has been described for Titanium White [47].

Intermediate layer

In other instances, in order to "receive" the coating, an" **intermediate layer"** which increses the functionality of the surface may need to be added to the pigment particle surface. As Bugnon (1996) reports, this is the case of organic pigments which, in order to receive an inorganic coating, need first to be treated with materials such as derivatives [36]. Pigment derivatives, also called synergists, are coloured non-polymeric compounds composed of a polar group and a structural element similar to the pigment molecule which provides strong adsorption on the surface. These are mostly used in organic pigments [40, p. 10; 36, p. 40]. The non-polymeric compound is oriented outward and is intended to improve the action of polymeric dispersants, however, their use may result in undesirable shifts in hue [16, p. 40].

Dispersants are mainly polymeric compounds, natural or synthetic, that act as dispersing agents. The structure can vary according to the distribution of the monomers (for example, statistical copolymer, random copolymer, block copolymer or graft copolymer) [37]. These compounds are generally deposited on the surface of the pigment through precipitation[9]. As explained by Farrokhpay (2004), polymeric dispersants are distinguished from inorganic or very low molecular weight organic dispersants because of their higher molecular weight. They bound to numerous surface sites at the same time forming durable adsorption layers on the particles. They contain an anchoring functional group or groups and the molecular weight must be sufficient to overcome van de Waals forces and anchoring groups must be firmly adsorbed on the particles surface [48].

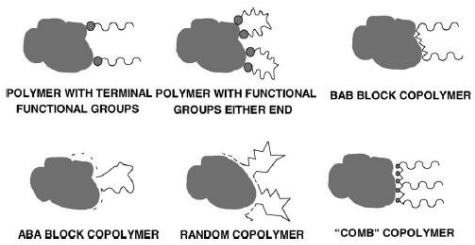


Figure 5. Schematic representation of different types of polymeric dispersants. (Illustration from Schofield 2002, p. 250 [49])

[8] According to Lu et al. (2009) "adsorption is the accumulation of matter at the interface between an aqueous solution phase and a solid adsorbent without the development of a three dimensional molecular arrangement. In other words it implies the formation of a two-dimensional molecular layer on the surface" [39, p. 99].

[9] According to Lu et al. (2009), a "precipitation reaction can form a mono-layer or a multi-layer adhesion" [39, p. 97].

Examples of surfactants that can be used as dispersing agents are cationic surfactants such as quaternary ammonium compounds [37, p. 321]. The “head” functions as an anchoring group which binds to the surface of the pigment through preferential adsorption[10] and the "tail” extends and is solvated in the binder. However, more commonly, surfactants tails are considered too short to provide steric hindrance[11] and other substances such as long-chain carboxylic acids (fatty acids) are added [49].

Post-synthesis: an additional treatment

After the coating is applied, pigments are washed, filtered and dried. During filtration the pigment is squeezed into a damp powder (“press-cake”) and during the process of removing the water, particles are subjected to compressive forces which cause them to aggregate and adsorb water (“hydrophilic aggregation”) [44]. In many cases the form or shape of the pigment is then achieved by grinding or milling coarser particles to a finer size. However, these procedures do not necessarily guarantee uniformity of particle size or shape required. As a result, when paint manufacturers receive the dry powdered pigment, the particles are agglomerated [44, p.123]. To prevent water absorption and reduce agglomeration of pigment particles during storage, various authors mention an **additional treatment during the final milling,** which is performed to break down agglomerates rather than to reduce particle size, with substances such as silicones, organophosphates, and alkyl phthalates [47, 43]. This final addition can occur both in the wet and dry state and is described as a “grinding aid” [43, p. 111]. The treatment is reported to “promote the processes of surface reactions or adsorption at the surface and enhance pigment wettability thus improving compatibility of the pigment with organic substrates, promoting a better dispersion of the pigment in the binder and its stability in the paint system” [42, p. 68; 43].

Additionally, as Braun et al. (1992) explains, when pigments are micronized (in a type of fluid-energy mill) the use of these substances can avoid that the pigment adheres to the conveying equipment and forms chunks and thus improves its dry-flow [43].

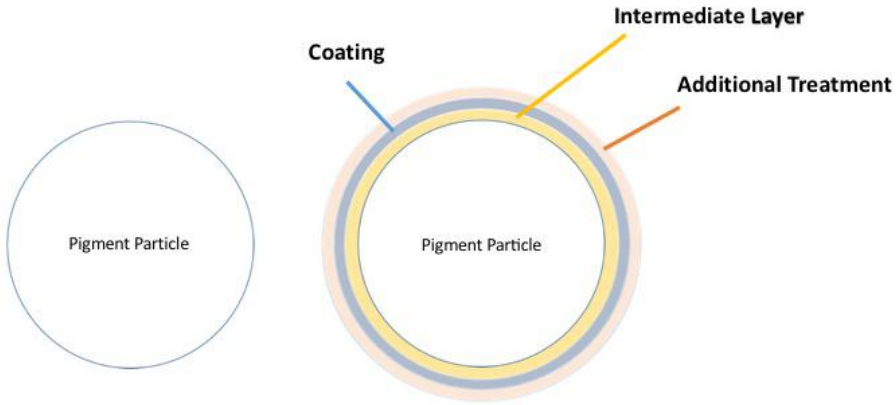


Figure 6. Pigment particle before and after surface treatment (diagram by the author)

1.2.2. Pigment surface treatments, paint manufacturing and paint defects

Pigment particles, depending on if they are inorganic, organic, white or coloured, can provide white or colour through light scattering and/or selected absorption of light [44]. For optimum efficiency of the paint formulation and to better achieve the desired effects, there are several important factors to be considered: pigment volume concentration (PVC), particle shape, and size and particle size distribution [44]. As Braun explains, the ideal particle size population for Titanium White so that the pigment can achieve maximum

[10] According to Lu et al. (2009), “adsorption refers to the accumulation of matter at the interface between an aqueous phase and a solid adsorbent without the development of a three dimensional molecular arrangement and implies the formation of a two dimensional molecular layer on the surface (e.g. chemisorption and specific adsorption)” [39].

[11] Steric hindrance, or stabilization, as defined by Napper is “a generic term that embraces all aspects of the stabilization of colloidal particles by nonionic macromolecules” [50].

light scattering (maximum hiding power[12] and opacity) is between 0.22 to 0.24 µm [43]. Manufacturing particles with sizes within this range is important because bigger particles may cause a light shift to red and smaller particles to blue, thus causing an undesirable "undertone" that can be visible in both coloured and white coatings when the hiding is incomplete [43].

The aspects mentioned above are primarily connected to the controlled synthesis of pigment properties (e.g. shape, size and size particle distribution). However, if a pigment is not correctly dispersed and stabilized in the binder, various paint short-comings and defects can result, such as poor application characteristics, the separation of phases and sedimentation [45, p. 75]. Also, changes in viscosity can be directly related to flocculation and this must be avoided not only during the production process but also during storage and application (see 1.3.1) [25, p. 436].

Pigment dispersion can be described as a three step process: wetting (a), dispersion/grinding (b), and stabilization (c). The figure below illustrates the three steps (see figure 7 below).

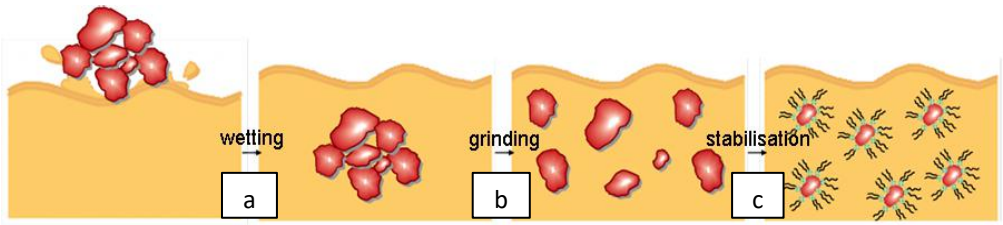


Figure 7. Dispersion process: wetting, dispersion/grinding and stabilization
(http://www.uniqchem.com/dispersing-technology/?lang=de…….)

(a) The first step is the incorporation of the pigment in the binder in a process called **wetting.** This process consists of the replacement of the pigment-air interface by a pigment-binder interface which is accomplished by the penetration of the binder into the spaces between the pigment particles [45, p. 70]. Depending on the character of the particle surface this process may be more or less difficult to accomplish. Organic pigments, for example, present smaller particle sizes which translates into a larger surface area [27]. After the pigment is wetted out, the mixture is ground and dispersed.

(b) During **grinding**, large pigment particles (agglomerates) are broken into smaller units, ideally into primary particles. At this stage, two important things happen: pigment particles are constantly moving and colliding with other pigment particles because of Brownian motion, an induced movement of particles in a liquid phase [25]. However, in the absence of repulsive forces (that is when the dispersion is not stabilized), particles have a tendency to attract, re-agglomerate and undergo *flocculation,* a type of particle aggregation that can be reversed by applying relatively low levels of shear [40]. This attraction can be explained due to the particles surface energy but also to the new active surfaces which are exposed during grinding [40, p.6].

(c) **Stabilization** of non-aqueous paint systems, like oil paints, occurs mainly through steric stabilization (also called entropic stabilization) a mechanism that explains the ability of certain substances to inhibit flocculation of suspensions [50]. These substances are mainly polymeric compounds, natural or synthetic, that act as dispersing agents[13], and whose structure can vary according to the distribution of the monomers (as noted above, examples are statistical copolymers, random copolymers, block copolymers or graft copolymers) [37]. These substances contain multiple anchor groups that adsorb and cover the particle's surface in such a way that their polymer tails form long loops which extend out into solution providing a barrier and thus an effective stabilization of pigment particles against flocculation (See below, figure 8). According to Schoffield (2007), these polymeric treatments, also called "hyperdispersants" were developed during the 70s and 80s [52, p. 5].

[12] According to Moezzi et al. (2012) "hiding power is the ability of a coating to mask the color of the substrate. It is related to the ability of a particle to scatter light, which in turn is directly related to refractive index. The average refractive index of rutile crystal (2.73) is considerably higher than that of ZnO (2.02)" [51, p. 14].

[13] Improvements in dispersion can also be achieved by inorganic treatments such as a coating of "fluffy" aluminum (see point 1.3.1)

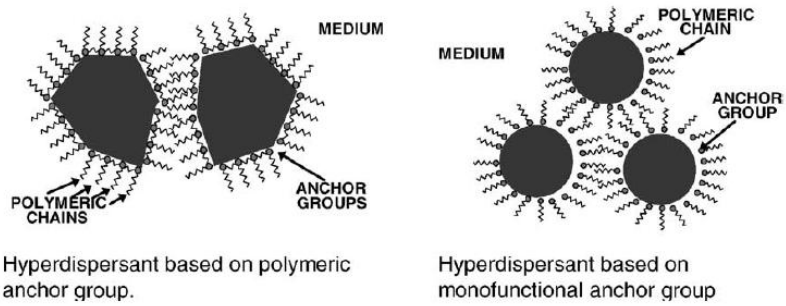


Figure 8. Illustration of pigment steric stabilization provided mechanism for two hyperdispersant configurations. (Illustration from Schofield 2002, p.250 [49])

Other treatments

Not all paint defects are solely connected to poor dispersion phenomena. As Bugnon (1996) notes "interactions occurring on the surface of the pigment are responsible for a number of properties, from dispersibility to photodegradation and thermal instability" [36, p. 39]. Pigment surfaces such as those in Titanium White can be reactive, with photocatalytic behavior; Titanium White pigments can induce the degradation of the binder and cause **chalking** [11]

When high hiding power or opacity is required, aside from being surface-treated with high volume metal-oxide layers for example, (where the precipitate acts as a spacer for the individual pigment particles), pigments such as Titanium White can be mixed with extenders which will act as spacers for the pigment particles (patent from 2014, 0000483 A1). Extenders such as $CaCO_3$ are known to be surface-treated, with fatty acids such as stearic acid [52]. But this may cause problems for the stability of paints, as hypothesised by Boon and Hoogland (2014) in their study on unstable, dripping paints: "carbonate extenders are not always clean and often treated with surface modifiers to increase wettability and flow so interaction and stabilisation of an extender surface can be inhibited" but less is understood about the "molecular level interaction of mineral components in paints including pigment and extenders with the organic materials" [53, p. 239].

1.3. White Pigments

Lead White, Zinc White and Titanium White are considered the most important white pigments for the 20th and 21st centuries. Their technology, methods of manufacture, history and identification have been described extensively in the literature and is therefore not repeated in detail here. It is however important to highlight some aspects of pigment manufacturing in order to link manufacture with surface treatments, and eventually to the pigments used in artist oil paints.

General information on pigment production technology can be found in the technical literature (see Pfaff 2017 [41]; Buxbaum and Pfaff 2005 [42], and Patton 1973 [54]). More detailed information regarding Lead White use in artist's paints can be found in Gettens, Kühn and Chase (1967)[55], and Eastaugh et al. (2008)[56]. Zinc White was recently investigated by Osmond (2014)[10] and the history and technology of Titanium White was reviewed by Winkler (2003)[47], Braun (1992)[43], and Laver (1977)[57], and as mentioned above, more recently by van Driel (2018)[11]. Lead White, Zinc White and Titanium White are all group names within the pigment industry and stand respectively for Pigment White 1 (PW1), Pigment White 4 (PW4) and Pigment White 8 (PW8) (Eastaugh 2008)[56].

1.3.1. Lead White

White Lead, basic lead carbonate ($2PbCO_3.Pb(OH_2)$), is the oldest white pigment in use today, and is also one of the oldest synthetically produced pigments [55]. It was the dominant white pigment in coatings for centuries, having performed well with linseed oil, the dominant binder until the 1930s. Due to its toxicity and increased health awareness during the 19th century, White lead found its use increasingly restricted

and legislated. By the 1970s, its use was prohibited in household paints, although not in artist's paints. Historically it has been used in skin plasters, ointments, in cosmetic goods and as a pigment [55, 56].

White lead occurs in nature in the form of the mineral hydrocerussite. The industrially produced pigment "is the synthetic analogue of the mineral hydrocerussite and consists of a mixture of cerussite, $PbCO_3$, and its hydrated form hydrocerussite, $Pb_3(CO_3)_2(OH)$, which can be found with different stoichiometry depending on the manufacture route" [55, 56, 58].

Until the nineteenth century the main manufacturing routes consisted of methods which involved the exposure of metallic lead to acetic acid fumes in a carbon dioxide rich environment mainly based on variations of the 16th century method known as the Dutch stack process [41, 58, 56, 59). Increasingly in the 19th century other methods were introduced that consisted of the aqueous conversion of oxides or soluble lead salts. Eventually electrolysis methods were introduced in the 20th century [41, 56]. These modifications in manufacture were developed in order to have more control of the synthesis process but also so that the process itself became faster and more economic [55, 58, 59].

Different methods of manufacture produce particles of different shapes, sizes and size distribution which result in differences in oil absorption and rheology [58]. According to research carried out by Campos (2010), the methods based on slow corrosion of the lead produce rounded particles with sizes ranging from 0.5µm to large aggregates of 20-65µm [58]. In contrast, the modern precipitated particles are described as thin plate structures with geometrical edges with more regular size (0.8 to 10 µm) [58]. Also, according to Gonzalez (2016) "morphologies (sizes and shapes) of cerussite and hydrocerussite crystallites can markedly vary" [59, p. 43].

Surface Treatment

Collecting information regarding the surface treatment of lead white proved to be challenging, this difficulty may be attributed to its decreased use or substitution within the industry due to its toxicity and subsequent changes in legislation governing its use.

The first record found for the surface treatment of Lead White pigments dates from 1911 in a patent from Ramage [60]. This was in response to complaints regarding the rapid disintegration and chalking of paint with lead pigments such as white lead which was brought about by the "formation of lead soaps with unsaturated acids of the linseed oil or other oil comprising the vehicle" [60, p. 1]. Ramage proposed various methods for the precipitation onto basic lead carbonate and lead based pigments with soluble organic substances such as soaps (e.g. sodium stearate), stearic acid, and bleached tallow by controlling the precipitation conditions (e.g. application of temperature). It was claimed in the patent that these materials would saturate the pigment and thus neutralize the pigment's reactive surface. Other claims for this invention include that the pigment would be readily miscible with linseed oil, suspend easily, and spread smoothly with the brush [60].

In other patent from 1932, Jones mentions the use of "protective colloids" (e.g. glue and gelatin) combined with a surface-active agent to control the precipitation process of lead white pigments produced via wet chemical processes to achieve the "desired size and other physical properties" [61, p. 3]. According to Jones, the pigment is precipitated in a solution: "basic lead may be precipitated from a solution of 5% of lead nitrate in the presence of a 3% solution of gelatin by adding a sufficient amount of sodium carbonate" and is subsequently separated from the protective agent in a centrefuge) [61, p . 4].

A patent from 1938 by Meister and Elizabeth describes treatments to improve wetting, dispersing and non-settling of pigments particularly lithophone but also other colored and white pigments such as Titanium white, basic lead carbonate, and extender particles with "water-insoluble organic compounds" such as "stearates of aluminum, lead, zinc, etc. and in particular the fatty acids of glycol"[33, p. 1].

In more recent times, it is increasingly difficult to find patents or specific references to the treatment of white lead pigments. Moilliet et al. (1969) mentions the addition of soaps [62, p. 291], and Schrödder (1988) specifies that "lead pigments such as lead chromate and lead molydbate are coated with layers of alumina, silica, aluminium hydroxide, silicon hydroxide, phosphates, polyphosphates, etc. in order to diminish the

concentration of soluble heavy metals and increasing its chemical inertness towards oxygen and Sulphur dioxide" [4, p. 6]. There is however no specific mention of lead white pigments being also treated with inorganic substances.

More recently, lead white was found mentioned in a patent from 2006 describing a treatment for improved processability and dispersibility in thermoplastic compositions [63].

Lead white in artists' oil paints

Modern lead white pigment used in artists' oil paints could consist of those produced with the traditional Dutch stack method or with modern wet chemical processes (see text below). According to Gonzalez et al. (2016), in the beginning of the 20th century artists preferred oil paints produced using the traditional Dutch stack process [59].

Lead White pigment can be found mixed with extenders such as calcite ($CacO_3$) and the pigment is sold both as a free flowing dry powder and as a paste in a binder (putty) (e.g. Kremer Pigmente© 460007 and 460027) (as was found listed, 14 September, 2018, on the Kremer Pigmente© website).

Examples of suppliers that currently manufacture lead white pigment using the traditional Dutch stack process are Michael Harding© and Natural Pigments© as was found on September 15, 2018, on the website of both manufacturers. Also as of 17 September, 2018, on the Kremer Pigmente website it can was found listed in their line "KREMER-made and historic Pigments" a Lead White, "Cremnitz White", but is unclear how the pigment is manufactured.

Regarding artist's oil paint formulations, Royal Talens©, report that due to lead white's toxicity they opted to remove lead compounds from their paints formulations "ten years ago" (as was found specified on September 14, 2018, on Royal Talens© website). Other paint manufacturers such as Winsor and Newton© (W&N) continue to produce it but sell it with restrictions (e.g Artist's Lead White paint is only available in tins in the EU) (as was found stated, 15 September, 2018, on the W&N© website).

Based on the information collected it is unclear if lead white pigments used in artists oil paints are or were ever modified. There is however the possibility that pigments produced via wet chemical precipitation have been treated with organic substances[14].

1.3.2. Zinc White

Zinc oxide (ZnO) was originally a byproduct of copper smelting used in the production of brass and was used for ointments until the mid of the 18th century when it was found that it could be obtained by the combustion of metallic zinc [41]. In 1781 its production as a pigment, Zinc White, began in France and, in 1840, Leclaire produced it on an industrial scale with the indirect or French processs [10, 51]. Compared to lead-based pigments, ZnO had the advantage of being non-toxic and non-darkening when exposed to sulfurous gases which led to its rapid spread [10].

Zinc oxide absorbs UV radiation and its surface is amphoteric, reacting with both acids and bases and being considered very reactive [42]. Due to these properties, in the second half of the 19th century ZnO was introduced in rubber as a vulcanization catalyst to reduce vulcanization times [10]. As noted by Moezzi et al. (2012) "the uses of ZnO have changed markedly over time" and, "today its major uses are in the rubber industry, followed by ceramics, but it has many niche applications such as, for example, in drilling fluids for the oil and gas industry" [51,p. 12].

Industrial grade zinc oxide is manufactured by any one of three methods: the French process (indirect), the American process (direct) developed in 1852, or the modern wet chemical process [41, 42]. According to Osmond (2014) the indirect French process produces a product which is more chemically pure and less

[14] While visiting the premises of Michael Harding's Artists Oil Paint in the early 2000s, a bag of lead white powdered pigment was shown to Leslie Carlyle that advertised the use of a lecithin based coating. Personal communication, Dr Leslie Carlyle September 2018.

stable [10]. Moezzi et al. (2012) reports that French process pigment particles can be described as nodular in shape with 01-5 µm [51, p.10], the direct American process produces a larger particle that can be described as acicular or needle-shaped with sizes ranging from 0.5-10 µm. According to Osmond (2014) the American process is reported to be more stable [10]. As for the wet process Moezzi et al. reports that it produces "a sponge-like form with porous aggregates being up to 50 µm diameter" [51, p. 10].

According to Buxbaum and Pfaff (2005) ZnO is sold in different grades which are differentiated by a quality designation, White, Green, Red, Gold and Grey "Seal." White Seal, is the purest > 99% ZnO, but with poor covering power; Green Seal is greater than 99% ZnO, but with higher covering power than White Seal; Red Seal is slightly less pure and generally used for painter's grounds; Gold Seal is similar to Red Seal, and Gray Seal contains some metallic zinc [42].

Surface Treatment

Technical literature describes Zinc Oxide surface treatments as an *aftertreatment* (see 1.3.1) [41, p. 85*;* 42, p. 80]. This can include different types of approaches: thermal treatment at temperatures up to 1000ºC mainly applied to ZnO produced by the direct method; coating the pigment particles with organic material (e.g. oil and propionic acid) to make the surface more organophilic thus increasing pigment particle wettability; and controlled atmospheric calcination to improve the photo-conducting properties of the high purity oxide use in photocopying [41, p. 85; 42, p. 80]. Thus, ZnO surface treatments improve the pigment weather resistance, lightfastness and dispersibility in most application systems [41,p. 85].

According to Moezzi et al. (2012), the primary market for early industrial Zinc Oxide was as a pigment for paints and as a catalyst for the rubber industry [51]. The earliest patent found was a US patent from 1938 which concerned the treatment of ZnO for incorporation in rubber. This patent proposes the use of protein materials such as "casein, glue, hemoglobin ,egg albumen, and glycine" to give improved properties in rubber dispersion [64]. Other patented substances listed by Barnett (1949) which claimed to improve the dispersion of ZnO in rubber, included propionic acid, and substances which were "fatty, naphthenic, abietic and other acids as well as soaps of these acids" [12].

Research by this author suggests that depending on the end use, Zinc Oxide surface reactivity was considered problematic. An early example is a patent submitted by Depew in 1942 describing the use of "polymerized, insoluble alkyd resins", such as urea-formaldehyde and glycerin phthalic acid, that "chemically combine" with the surface and form an "inert coating" that does not dissolve or react when embodied in the paint [65]. Depew notes that previous inventions mention the use of "fatty acids, various organic materials and alkalis" [65]. Depew states that these treatments do not make the surface less reactive nor are the coatings themselves inert [65]. In 1949, Barnett reports a zinc phosphate coating to "retard reactivity with the weak organic acids in the paint vehicle" [12, p. 277].

Zinc White in artist's oil paints

According to Osmond (2014), zinc oxide was first listed as an artist pigment by Winsor & Newton in 1834 as a watercolor pigment called Chinese White but its first appearance in oil tubes dates from 1860, or even earlier [10]. As Osmond notes, according to Carlyle's research (Carlyle, The Artists Assistant 2001 [66]), although not declared, ZnO was already being incorporated in paints [10]. Also, according to Osmond (2014), for artist's paints, historically both indirect and direct processes have been used [10]. Nowadays the French process, although less stable is preferred due to its high purity [10, 51].

In the patent research carried out for this investigation, surface treatments for ZnO can be found starting in 1938 (see text above).

Research based on data-sheets from artist pigment suppliers such as Kremer Pigmente©43600 show that Zinc Oxide is listed as appropriate for incorporation in different media such as "acrylics, Lime / Fresco, Ceramic, Oil, Tempera, Watercolor / Gouache, Cement / Tadelakt." However the manufacturing method for the zinc oxide is not given as can be seen, as of September 21, on the suppliers website.

Regarding Zinc White used by artist oil paint manufacturers, the pigment can be found sold as a single colour paint but also as an "additive" to counter yellowing with Titanium White and Lead White. Examples of this can be found listed in Natural Pigments website © where, as of September 9, 2018, there is a table which "lists the pigments and drying oils included in commercial oilpaint when these components were identified on the label by the manufacture" (https://www.naturalpigments.com/artist-materials/zinc-white-oil-paint-color/).

Judging from the use of industrially produced pigments in artist's oil paintings in general, it would not be surprising to find zinc oxide pigments which were modified for other coating systems or media being used in artists' oil paints.

1.3.3. Titanium White

Titanium dioxide (TiO_2) was first introduced in the 19th century but it was only in the beginning of the 20^{th} century that it found use as a new synthetic white pigment (Titanium White). TiO_2 occurs in nature in three crystalline forms: brookite, anatase and rutile. From these only anatase and rutile are commercially relevant. These differ in lattice structures, refractive indices and densities [43]. There are two main routes of manufacture, the sulfate route, first developed in 1919 producing both the anatase and the rutile form, and the Chloride route which was developed in the 1950s (by DuPont©) and which produces mainly the rutile form [43, 11, 57]. Both Anatase and Rutile are "strong absorbers in Ultraviolet light (UV light) and are photochemically active, meaning that the absorption of light can lead to chemical reactions" [11].

Titanium White pigments are typically 150-300 nm in size, rutile crystals are described as stubby needles and the anatase crystals as thick platelets [67].

Surface Treatments

Due to its importance in industry, Titanium White surface treatments have been very well developed. Mentions regarding the surface treatment of Titanium White can be found in the pigment technology literature and in academical research (e.g. [[11], [67], and [48]). The background provided by Laver (1977) and Braun et al. (1992) deserves particular attention [57, 43].

The treatment of TiO_2 is usually referred to as an *aftertreatment* and the procedure is described, similar to what has been explained above (See 1.3.2), as consisting of an inorganic treatment which is applied in an aqueous slurry or in a dry form, with a secondary organic treatment, that can consist of up to 1% of the dry weight of the pigment [57].

The inorganic treatment usually consists of hydrated oxides which are precipitated with materials such as alumina, silica, zirconica, phosphorus, boron, barium, zinc and tin compounds, and/or small amounts of cerium, chromium, manganese, and cobalt compounds. These treatments are applied for multiple reasons [43, 57].

The organic treatments usually consists of a polyol, an amine, silane or siloxane that are applied to modify dispersion properties depending upon the final application [48, p.25, 43]. Common polyols are pentaerythritol, trimethylol propane, alkylene oxides, high molecular weight condensation products of alkylene oxides with amines, phenols, long-chain fatty alcohols [43, 57].

Braun et al. (1992) provides a systematic overview of "coated pigments in the market": uncoated, which are used in plastics and paper, and coated, the preferred option for coatings. The latter are generally wet treated so that pigments are more easily dispersed in liquids of low or moderate viscosity. The coated pigments are further subdivided into interior grades and durable grades. Interior grades have up to 5% of hydrous alumina for ease of dispersion and the durable grades contain 2% silica but also oxides of zirconium, boron zinc, cerium, and tin, usually in concentrations of less than 1% [43]. Depending on the end use there are many different combinations of substances and methods of application [19]. For instances, for extreme exposure, rutile grades are encapsulated in glassy silica sheaths by methods such as the Dense Silica method developed by Iler (1969) [68].

Veronvski (2014) reports that another way to distinguish treatments is that they are dense for paints and plastics, porous for emulsion paints, and lightfast with a dense coating for the paper laminate industry. Highly-weather resistant types are coated with up to 15% silicon dioxide (SiO_2) or zirconium oxide (ZrO2) and treatments are commonly precipitated in layers [46].

When investigating the titanium dioxide pigments for the presence of surface treatments it is important to note that these pigments after manufacturing are not simply titanium and oxygen [11, 67]. During crystallization insoluble compounds accumulate on the surface. These can be impurities from the ore such as iron, or additives designed to control crystal structure and growth [43, p. 117; 57, p. 11; 67]. By a close reading of the different descriptions it may be possible to anticipate the type of treatment, thus linking analytical results with the literature.

Originally Titanium White pigment was treated to improve durability (by reducing chalking) and to reduce the yellowing that occurred in certain kinds of paint. Treatments were also applied to prevent fading when mixed with coloured pigments. Subsequently it was found that the correct choice of coating could be used to improve the dispersibility of these pigments in all media. [57]. Other concerns reported for early paints containing TiO_2 were stiffening, settling out, and the formation of hard cakes (e.g. as described in patent by Gardner in 1933) [32]).

Titanium White in artists's oil paints

As reported by van Driel (2018) "titanium white paints exist in a wide range of formulations, they can contain a combination of zinc white, extenders such as $CaCO_3$ or $BaSO_4$, additives (e.g. metal stearates or drying agents) and the binder" [11, p. 190]. Also, according to van Driel's research "photocatalytically active titanium dioxide pigments have been, and still are, widely present in the pigment market" [11, p. 233]. Van Driel notes that such titanium dioxide pigments have been finding their way into "artist paints, restoration materials and industrial paints (which are also used in works of art), posing a serious threat to 20th century restoration works and 20th century art objects" [11, p. 233].

2. Experimental design

In this thesis, a combined multi-analytical approach was followed that aimed to enable the investigation of both the organic component and inorganic component of the surface treatments on unbound pigments. As was described in PART I, the first step was to carry out a literature search. This step is fundamental in order to have references reagarding treatments and materials and thus be able to identify substances as surface treatments. This is particualraly relevant when investigating the organic component. Techniques were selected based on their suitability. Hyphenated mass spectrometry techniques were proposed for the investigation of organic components and Electron microscope techniques for the investigation of inorganic components. The equipment used is detailed in Appendix II, and the data produced is detailed in Appendix II, IV, and V. SEM-EDX analysis were performed and interpreted by Cátia Ferreira.

2.1. Description of Pigment reference material

A total of sixteen samples of unbound pigments were collected: five Lead White, six Zinc White and five Titanium White. Most samples were collected from the RCE reference pigment collection (Table 1). This collection holds a large number of pigment sample material from different sources that includes donations by institutions, acquisitions from various sources such as contemporary artist's pigments manufacturers and houses historical pigments no longer available due to their toxicity. It is important to note that there were different amounts of information available about the provenance of these pigments, and some had previously been studied.

Regarding the **Lead white** pigments, three samples were collected from the RCE reference pigment collection and two from the Carlyle MOLART Fellowship. The Schoonhoven sample is a modern process Lead White pigment from a Dutch source, purchased in 1999 from Schoonhoven, and the Kremer pigment sample was also acquired in 1999 from Kremer Pigmente© [17]. As to the **Zinc White** pigments, all were selected from the RCE pigment reference collection save one, which was provided by Leslie Carlyle (Zinc White Carlyle, pre-1980's). The **Titanium White** pigments collected were selected from sample material previously investigated in Birgit van Driel PhD research (2018)[11]. The selection include three anatase pigments and two rutile, the pigments are all contemporary and were acquired from different sources (Table 2).

Table 1. Lois Datebase information on pigment source/date from RCE pigment collection

Pigment	RCE code	Source	Date of incorporation at RCE
Lead White	8233	Dr. A. Haagen, Roermond	2004
	9612	Scheveningen Classic, Old Holland	2014
	9641	Sikkens Chest Nr. 1	2014
Zinc White	0191	Kremer Pigmente©, cat nº46300	n/a
	9496	n/a	n/a
	8232	Old Holland-Classic colors	2004.11.12
	9647	Sikkens chest, Nr. 7	2014.01 29
	9648	Sikkens chest, Nr. 8	2014.01.29

Table 2. Titanium White pigment sample selection and their characteristics, results from van Driel [11, p.114]

Code	Name	Description Based on previous studies or other available information	Year/period of synthesis	Employed synthesis method (manufacturer)
A1	Hombitan LW	Uncoated anatase	contemporary	n/a
A2	Huntsman A-HRF	Organically treated to promote dispersion	contemporary	Sulphate process
A3	Huntsman A-PP2	Treated with 2% A2O3 and 1% SiO2 + Polyol	Contemporary	Sulphate process
R2	Huntsman HDCD	Organically treated to promote dispersion	contemporary	Sulphate process
R3	n/a	Purchased at Dutch "verfmolen de Kat" in 2011	contemporary	n/a

3. Results and Discussion

3.1. Lead White

From the literature review it was found that Lead White pigments are treated, mostly with mettalic soaps and other organic material (see 1.4.1). The pigments in analysis come from different sources. Table 3 below summarizes the results of tests and analyses carried out on Lead White pigment samples.

Table 3. Summary of the Lead White pigments investigated and the techniques used

Samples	SEM-EDX	FEG-SEM	(S)TEM-EDX	EGA-MS[1,2]
8233, (2004) Dr. A. Haagen, Roermond	C, O, Al, Pb, S	n/a	N	acetic acid (**60**, 45, 43), Tº 250-350 ºC SO_2 m/z 64, 48
9612, (2014) Scheveningen Classic, Old Holland	C, O, Al, Pb, S,	n/a	n/a	SO_2 m/z 64, 48
9641, (2014) Sikkens Chest Nr.1	C, O, Al, Pb, S,	n/a	n/a	acetic acid (**60**, 45, 43), Tº 250-350ºC SO_2 m/z 64, 48
Kremer Pigmente ©,(1999)	C, O, Al, Pb, S	N	N $CaCO_3$ Silicate	SO_2 m/z 64, 48
Schoonhoven, (1999)	C, O, Al, Si, Pb, S	N	N	acetic acid (**60**, 45, 43), Tº 250-350ºC SO_2 m/z 64, 48

Notes: 1: The thermal behavior was detected and classes of compounds are described through molecular and fragment ions; T describes Temperature range of desorption and formation of chromatograms.
2: The most prominent peaks are represented of characteristic fragment ions.
n/a: Not available, N: None or not significant
Carlyle MOLART Fellowship pigments

SEM-EDX back-scattering imaging in LV mode was acquired enabling an initial screening of the pigment particle shapes and sizes (Appendix III, fig. 4). Images were compared, and it was observed that the pigment particles from different samples had different particle size ranges and shapes. The low resolution of these images and the different states of particle agglomeration did not, however, enable more detailed conclusions regarding particle morphology.

The analysis of SEM-EDX spectra (see above table 3, and Appendix III fig. 5) showed the presence of Sulphur (S) and Aluminum (Al) in all samples. In the Schoonhoven sample, a small trace of Silica (Si) was detected which may be attributed to contamination or to the presence of a SiO_2 crystalline extender [59].

FEG-SEM, was carried out on the Schoonhoven and on the Kremer Pigmente sample. Figure 9, below, indicates the difference between the Kremer Pigmente and Schoonhoven pigments. In these images there was no indication of a surface treatment, however a more detailed comparison between the morphology of the Kremer Pigmente particles and Shoonhoven particles was possible with this technique. The Kremer Pigmente sample (fig. 9 a) appears to be smaller and more “broken” than the Schoonhoven particles (fig. 9 b). These differences may be attributed to different manufacture processes (see 1.4.1. and [58]).

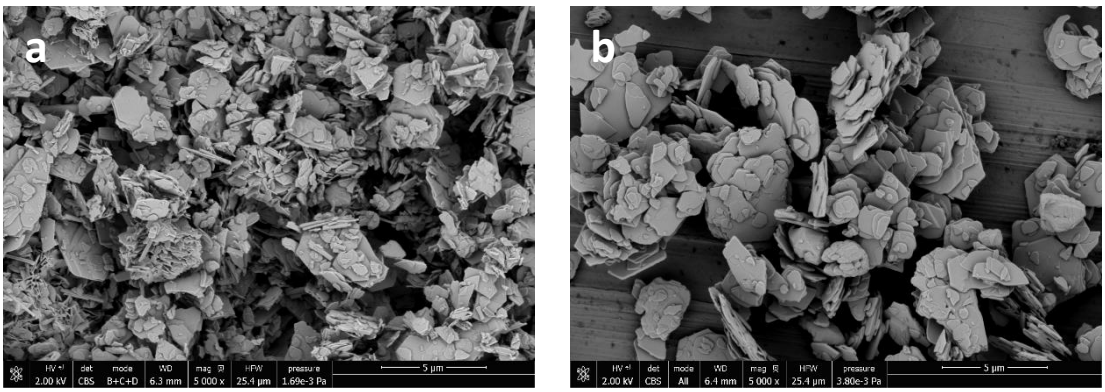


Figure 9. FEG-SEM images in CBS mode (5.000 x magnification) showing **a**) Kremer Pigmente and b) Schoonhoven, results acquired by by Ineke Joosten, conservation scientist at RCE. In **a)** Kremer Pigmente particles appear to have a more diverse range of particle sizes and shapes when compared with **b)** Shoonhoven, where particles appear to be less fragmented, larger and the edges more rounded, and less sharp. For more details see Appendix IV.

(S)TEM-EDX was carried out on three samples: on Kremer Pigmente and Shoonhoven from the Carlyle MOLART Fellowship, and on sample 8233 from the RCE reference pigment collection. Phase-map analysis results on the Schoonhoven sample shows a variety of materials present, including organic materials such as N, C, S, & K (see fig. 10. below, Appendix V fig. 21). It also confirmed the absence of visible evidence of an inorganic coating.

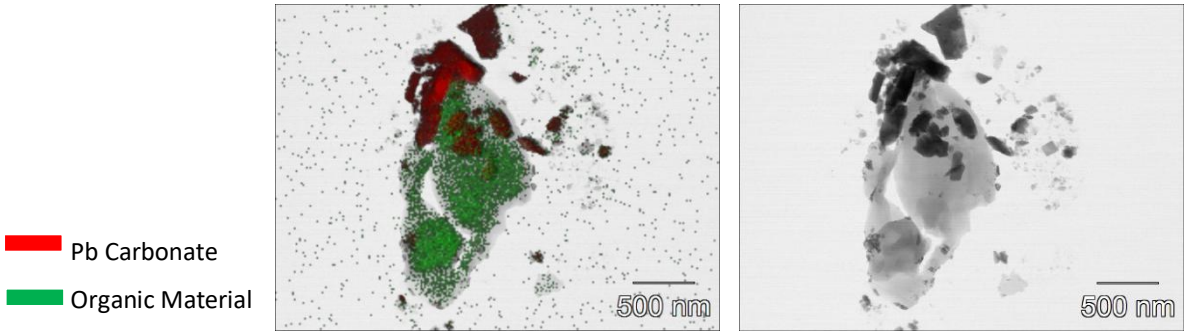


Figure 10. (S)TEM-EDX phase-map results of Lead White sample, Schoonhoven, from the Carlyle MOLART fellowship. In red we can see a phase rich in Pb Carbonate and, in green, a phase rich in organic material consisting of N, C, S, K and O. Analysis and results were provided by AKZO NOBEL Chemicals.

As for the Kremer Pigmente sample, the phase-map analysis results shows the presence of $CaCO_3$ and silicate, and some organic material (N, C and O). As seen above, the presence of $CaCO_3$ and silicate is not uncommon in Lead White pigments and could suggest the presence of an extender (Appendix V fig. 22). To note that Si was not detected with SEM-EDX (Table 3 above, and Appendix III< fig. 5).

Closer inspection and comparison of (S)TEM-EDX images in Bright Field (BF) emphasized the morphological differences between these three pigments (see below fig. 11 **a**, **b** and **c**). From their SEM images neither appeared to be Dutch stack process. Regarding sample 8233 from the RCE pigment reference collection, the presence of material which formed small dots on the surface of the particles was observed (below, fig. 11 **c**, and Appendix V, fig. 23 for more closer details). The phase-map analysis showed the presence of Fe, Zr, Co, Si, but no coating or material that could be linked to a surface treatment was clearly visible (see Appendix V fig. 24).

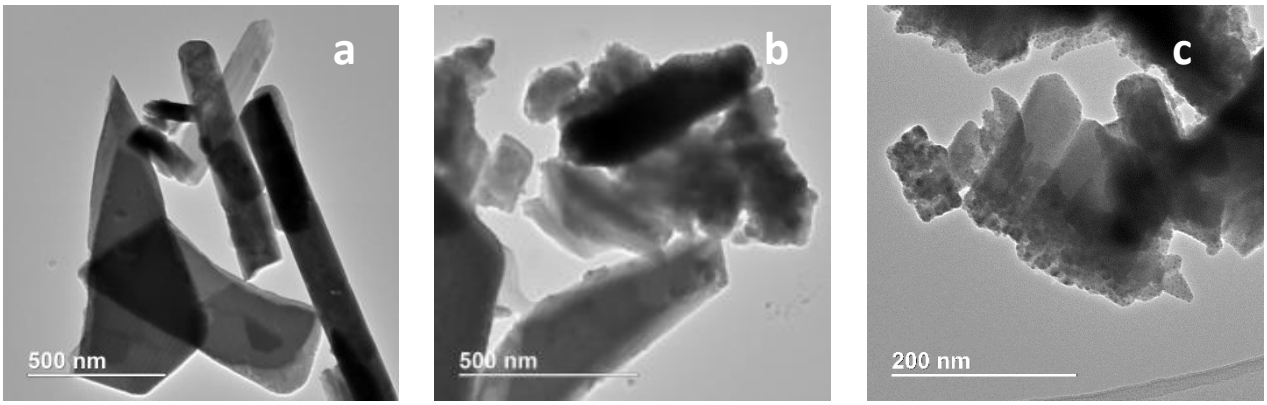


Figure 11. (S)TEM-EDX images with Bright-Field (BF) showing **a)** Kremer, **b)** Schoonhoven and **c)** 8233. Analysis and results were provided by AKZO NOBEL Chemicals.

Regarding the organic analysis, EGA-MS did not provide evidence of a surface treatment. However, Sulphur Dioxide (SO_2) which is a common contaminant was found adsorbed on all pigment surfaces (see text 1.3). Also, traces of acetic acid were identified, in samples 8232, 9641 and Schoonhoven. Acetic acid (vinegar) is used during manufacture to induce the conversion of metallic lead to lead carbonate during the traditional processes (see text 1.4.1).

Py-GC/MS was performed on sample 8233 however results were not significant and therefore they are not shown.

3.2. Zinc White

The literature review indicated that ZnO pigments may have at least an organic treatment. As noted above, the selected pigments had not been studied before and there are little information besides their source (the selected ZnO pigment samples and their sources are mainly paint manufacturers such as Sikkens, Old Holland, or Kremer Pigmente). Table 4 below summarizes the results of tests and analyses from the organic and inorganic analysis carried out on the selected Zinc White pigment samples.

Table 4 Summary of the Zinc White pigments investigated and the techniques used.

Samples	SEM-EDX	FEG-SEM	(S)TEM-EDX[3]	EGA-MS[1,2]	Py-GC/MS	Py-GC/MS TMAH
Carlyle (Pre-1980's)	C, O, Zn	Inc	Inc	Inc	Inc	Inc
0191,n.d., Kremer Pigmente© cat nº46300	C, O, Zn, Al	n/a	Inc	Inc	Inc	Inc
8232, (2004.11.12) Old Holland-Classic colors	C, O,Zn, Al	n/a	Inc	Inc	n/a	n/a
9496, (n/a)	C, O, Zn, Al	n/a	n/a	Inc	n/a	n/a
9647, (2014.01 29) Sikkens chest, Nr. 7	C, O, Zn, Al	N	Inc	Inc	Inc	Inc
9648, (2014.01.29) Sikkens chest, Nr. 8	C, O, Zn Al, S	n/a	n/a	SO_2 (64, 48), T° 500-700°C	Inc	Inc

Notes: 1: The thermal behavior was detected and classes of compounds described through molecular and fragment ions; T describes Temperature range of desorption and formation of chromatograms.
2 Selected most prominent peaks represented of characteristic fragment ions.
3 Bright Field
N: No coating, n/a: Not available, Inc: Inconclusive
Leslie Carlyle private collection

SEM-EDX back-scattering imaging in LV mode was acquired enabling an initial screening of the pigment particle shapes and sizes (see Appendix III fig. 6). By comparing the appearance of these particles they appear to be very similar and in the overall, very fine, homogeneous, and tending to form small clusters. In sample 9648 small white dots can be observed (see below fig. 12). These suggest the presence of a different material in the sample however SEM-EDX analysis does not reveal the presence of extenders. To date these small particles remain unidentified. The low resolution of these images did not enable more detailed conclusions regarding particle morphology.

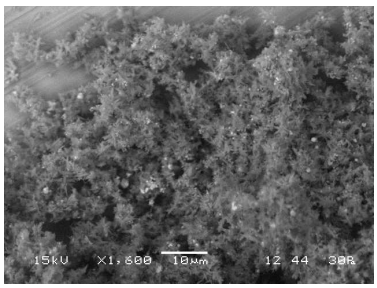


Figure 12. SEM-EDX image in LV mode (5.000 x magnification) showing ZnO 9648, small white particles are visible. Image acquired by Cátia Ferreira**.**

SEM-EDX analysis showed the presence of Alumina (Al) in all samples, Carbon (C) was detected in all samples save one, sample 8232, and Sulphur (S) was identified in sample 9648 (see table 4 above and Appendix. III).

FEG-SEM analysis was carried out on pigment sample 9647 (RCE pigment reference collection) and on the Carlyle pigment (see below fig. 13). By comparing the appearance of these particles in figure 13. **a** and figure 13. **b**, they are very different. While the particles in 9647 are plate-like with sharp edges, the Carlyle particles are more rounded. According to the descriptions provided by the literature (see 3.2), this may suggest that pigment 9647 was manufactured by the American process and the Carlyle pigment by the French process [51]. This observation appears to be confirmed by comparing the FEG-SEM image (fig. 13 b) with SEM images of particles obtained by the French process (fig. 13 c). However further investigation and comparison of samples with known manufacturing methods is needed to be able to draw any firm conclusions.

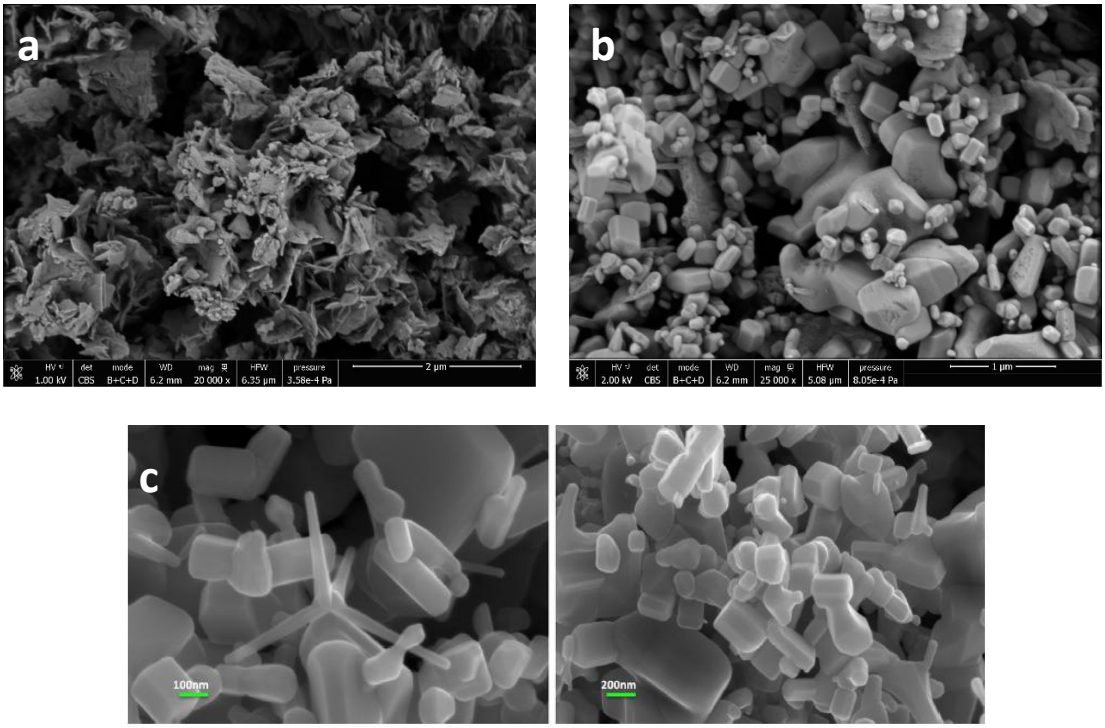
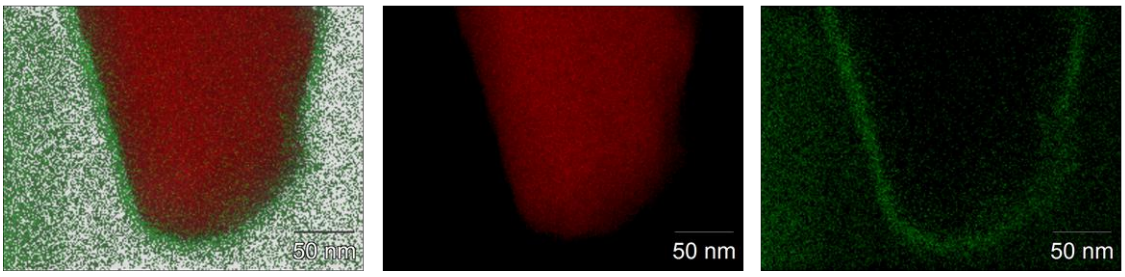


Figure 13. Above, FEG-SEM images in CBS mode showing a) 9647 (20.000 x magnification) and b) Carlyle (25.000 x magnification). Images acquired by Ineke Joosten. Below, c) SEM image obtained from the French Process [51,p. 4].

(S)TEM-EDX was performed on the Carlyle pigment sample, and on samples 0191 and 9647 from the RCE pigment reference collection. Analysis of the phase-maps on the Carlyle pigment (fig. 14, below) reveals the presence of a Silica-rich phase concentrated around the ZnO phase which suggests

the presence of an inorganic silica treatment. As for 0191 and 9647 there was no evidence for a coating on the pigment particles (see Appendix V fig. 26 and fig 27).



Element	ZnO	±	SiO_2	±
O	12.2	0.5	39.5	1.0
**Si	0.3	<0.1	11.2	0.7
Cl	0.3	<0.1	2.4	0.3
Zn	87.3	0.4	46.8	2.9

* C content in phase 2 is ~ 98 wt.%
** Si may derives from contamination

Figure 14. (S)TEM-EDX phase-images of ZnO Carlyle sample. In red we can see a phase rich in ZnO and in green a phase rich in SiO_2 in a thin line surrounding the particle, analysis and results were provided by AKZO NOBEL Chemicals.

Also, by comparing (S)TEM-EDX spectral images 0191 and Carlyle particles appear to be more similar when compared to 9647 particles, which are less round and more fragmented however these differences may be attributed to sample preparation (see below fig. 15).

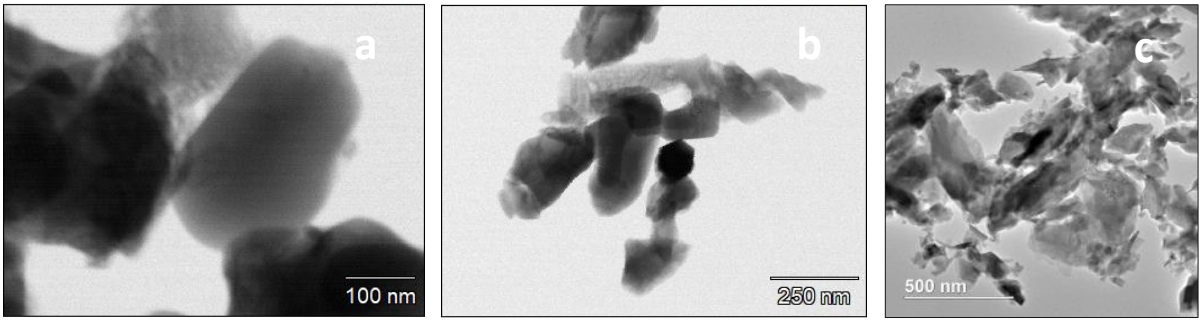


Figure 15. (S)TEM-EDX images of Zinc White pigments showing a) Carlyle, b) 0191 and c) 9647. Analysis and results were provided by AKZO NOBEL Chemicals.

Regarding the investigation of the organic component using EGA-MS analysis, this technique did not provide significant results. Sample 9648 showed the presence of Sulphur Dioxide, SO_2, (m/z 64), evolving at high temperature (500-700°C) which matches the Sulphur (S) previously identified with SEM-EDX (see text above). According to Osmond (2014) the presence of SO_2 on Zinc Oxide surface may be explained by a number of reasons: active surface and conversion to carbonate or sulphide may take place on ambient storages, direct process zinc oxide produces sulphur dioxide (SO_2), and complex sulfites and sulphates may form on the pigment surface [10].

Py-GC/MS with and without derivatization with TMAH, was carried out on three samples (Table 3). While Py-GC/MS did not reveal significant results, Py-GC/MS with TMAH showed very small traces of propionic acid. As previously mentioned (see 1.4.2), propionic acid is a known to be a coating treatment for zinc oxide pigments intended for incorporation in rubber. Patent research also revealed that zinc oxide pigments treated with this material are recommended for use in coatings and other non-aqueous media. In this case the intensity of the peak was very low and the absence of other significant results that could be linked to a surface treatment suggests that these samples were not organically treated.

3.3. Titanium White

The literature review indicated that the treatments for Titanium white are complex and can involve combination of both organic and inorganic treatments. As noted above, the titanium dioxide pigments selected for this investigation were previously characterized by van Driel (2018) and their surface treatment was investigated [11]. Table 5 below summarizes the results obtained from the organic and inorganic analyses carried out on the selected Titanium White pigment samples.

Table 5. Summary of the Lead White pigments investigated and the techniques used.

Samples	SEM-EDX	FEG-SEM	(S)TEM-EDX[3]	EGA-MS[1,2]	Py-GC/MS[2]	Py-GC/MS TMAH[2]
A1, (2017) Hombitan LW	C, O, Al, Ti	N	N	Inc	Inc	Inc
A2, (2014) Huntsman A-HRF	C, O, Al, Si, Ti	n/a	N	Inc	Inc	TMP (polyol)
A3, (2014) Huntsman A-PP2	C, O, Al, Si, Ti	Inc	SiO_2 and Al inorganic coating	Inc	2-ethylacrolein Cyclopentanone	TMP (polyol) 2-ethylacrolein Products from Glycerols: Propane, 1,2,3, trimethoxy Diethylene glycol dimethyl ester
R2, (2011) Huntsman HDCD	C, O, Al, Ti	n/a	N	Inc	2-ethylacrolein	Phenol, 2, 4-bis(1,1-dimethylethyl) (Antioxidant) 1,2-dimethyl phthalate (Phthalate) TMP (Polyol)
R3, (2011) Verfmolen de Kat	C, O, Al, P, Ti	n/a	Zr and Al inorganic coating.	Inc	2-ethylacrolein	(?) – identified Polyol Fatty acids

Notes: 1: The thermal behavior was detected and classes of compounds described through molecular and fragment ions; T describes Temperature range of desorption and formation of chromatograms.
2 Selected most prominent peaks represented of characteristic fragment ions.
3 Analysis performed by AKZO Nobel for Birgit van Driel. Data was previously published in her PhD (2018).
N: No coating, n/a: not available, Inc: Inconclusive results, TMP: Trimethylolpropane

In this study SEM-EDX analysis identified the presence of Carbon (C) in all samples, Silica (Si) was identified in sample A2 and A3, and Phosphorus (P) was identified in sample R3 (see table 3 above, and Appendix III, fig. 9 and fig. 10). The presence of Silica (Si) in A3 can be attributed to the coating (as was identified with (S)TEM-EDX)), however the A2 sample is reported to be uncoated therefore the presence of Silica is unclear. As for P, van Driel had identified this element with ICP-OES analysis[15] [11]. The detection of this element may be explained by the fact that P is an additive which influences crystal growth, it is not incorporated into the crystal structure remaining on the surface [43, p.109].

The analysis of the images obtained by backscattering imaging in LV mode (see figure 17, Appendix III) gave no further insights. The resolution is too low and therefore particle examination was not

[15] During ICP-OES analysis van Driel (2018) noted that although this technique is not localized it allows to quantify bulk material, but also analyze inorganic coatings [11, p.118].

possible. Furthermore, observation of pigment packing and agglomeration was too similar to draw conclusions.

(S)TEM-EDX results, provided by van Driel (analysis were carried out by AKZO NOBEL chemicals), showed that pigments A3 and R3 are inorganically coated (see below fig. 16, and Appendix V fig. 28 and fig. 29), and pigments A1, A2 and R2 can be considered uncoated (see above table 5,) [11, p.117-119]. It is interesting to compare inorganically coated and uncoated pigments (see Appendix V, fig. 29 **a)** and **b)**) but also to compare them with an example of what is described as an "unsuccessful coating" (see Appendix V, fig. 30).

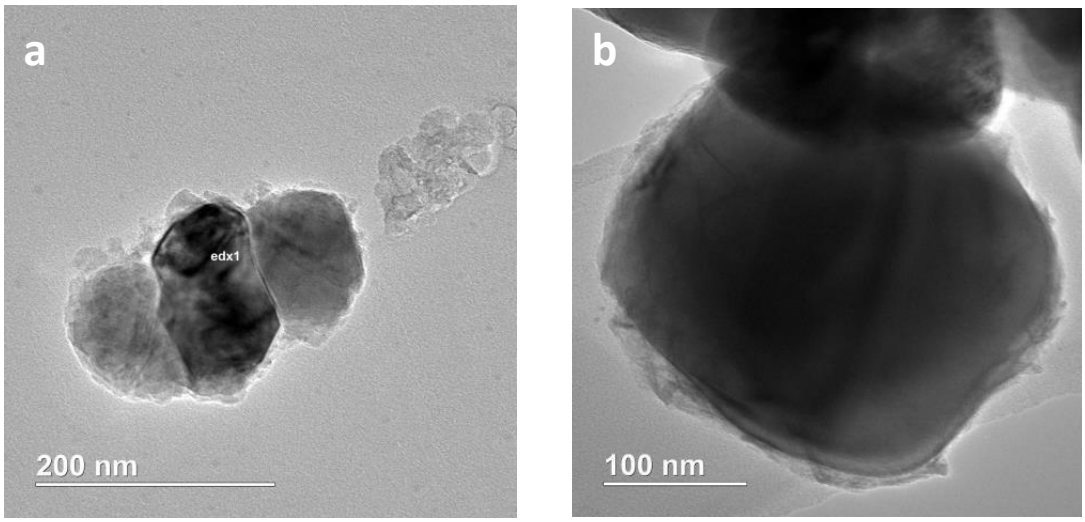
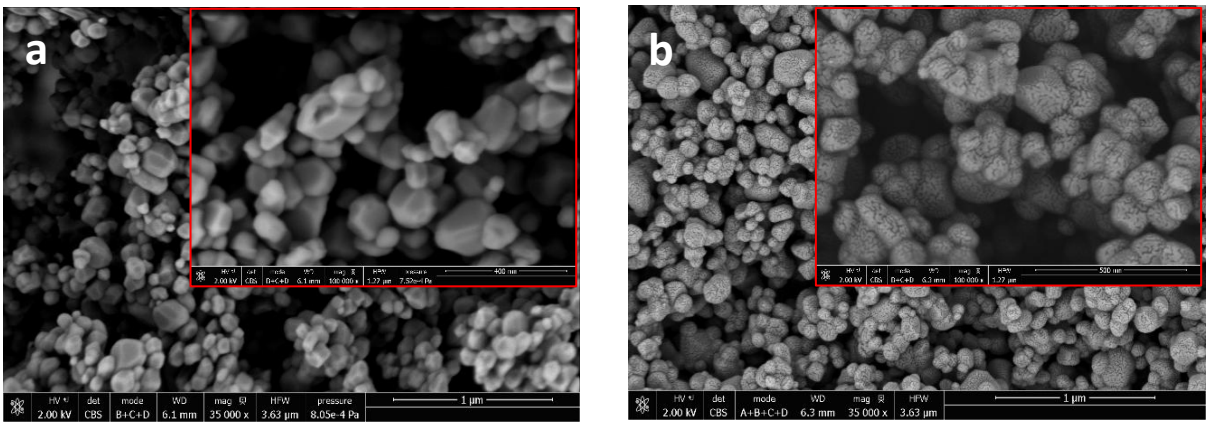


Figure 16. S)TEM-EDX images of inorganically treated Titanium White pigments showing a) A3 and b) R3. Analysis were carried out during van Driel's investigation [11] and results were provided by AKZO NOBEL Chemicals.

FEG-SEM was carried out on sample A1, the "uncoated" reference, and sample A3 which had been previously coated with gold (for SEM-EDX High Vacuum analysis). Even so, by comparing the images it is possible to see that both pigments particles can be described as "rounded" not being clear if they correspond to the provided description of "stubby needles" for anatase pigments (1.4.3) (see below fig. 17). Due to the gold coating on A3 it was not possible to observe "directly" the pigments surface and verify if the inorganic treatment could be detected. However, the coating with gold produces a morphology which appears to be very similar to what was found in a Ultramarine sample that was analyzed in Ferreira's pigments surface treatment investigation (figure 17 c) [19]. New analysis should be performed in order to verify if the coating in A3 can be observed, and if so, compare A3 with A3 gold coated, and the coated ultramarine blue pigment.



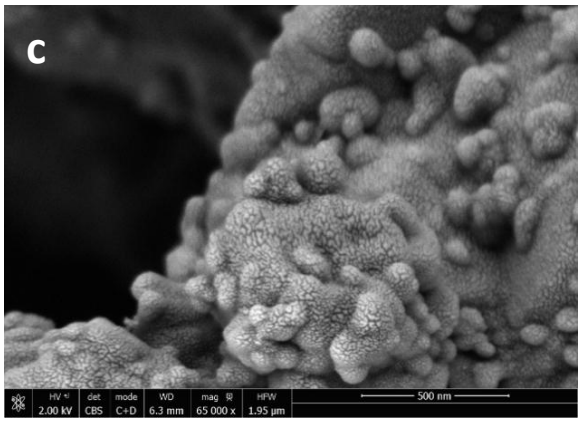


Figure 17. FEG-SEM images in CBS mode showing, a) A1, uncoated reference sample, b) A3 gold coated, c) Kremer Pigmente© Ultramarine blue, results acquired by by Ineke Joosten, conservation scientist at RCE.

As for the investigation of the organic fraction of these treatments, preliminary research performed by van Driel (2018) reasoned that A1 was unlikely to be coated, A2, A3 and R2 had most "likely a polyol", and , R3 was "likely" to be coated [11, p.120].

EGA-MS analysis were inconclusive regarding the presence of an organic surface treatment however, further investigation with Py-GC/MS, with and without TMAH, enabled the detection and identification of polyols on samples A2, A3 and R2 thus confirming van Driel's results [11] (see above table 5). Inez van der Werf, conservation scientist of the Rijksmuseum, assisted in the interpretation of pyrolysis data and identified the polyols as Trimethylolpropane (TMP). According to the literature TMP is a common polyol used as a grinding aid (see text 1.4.3). Regarding R3, a polyol was also detected but further work is needed in order to achieve a precise assignement.

Additionally, analysis revealed the presence of glycerol products (Propane, 1,2,3, trimethoxy and Diethylene glycol dimethyl ester) on sample A3 and 2-ethylacrolein on A3, R2 and R3. Regarding the glycerol pyrolysis products more information is needed in order to draw conclusions. Glycerol can be linked to many different compounds [16] remaining unclear its role in the pigment.

As for 2-ethylacrolein detected in the A3 (see fig. 18) and R3, its presence was found significant because although it was not possible to find information linking this compound to surface treatments it appears in the manufacturers (Huntsman) safety data-sheet, as a product of TiO_2 thermal decomposition [70].

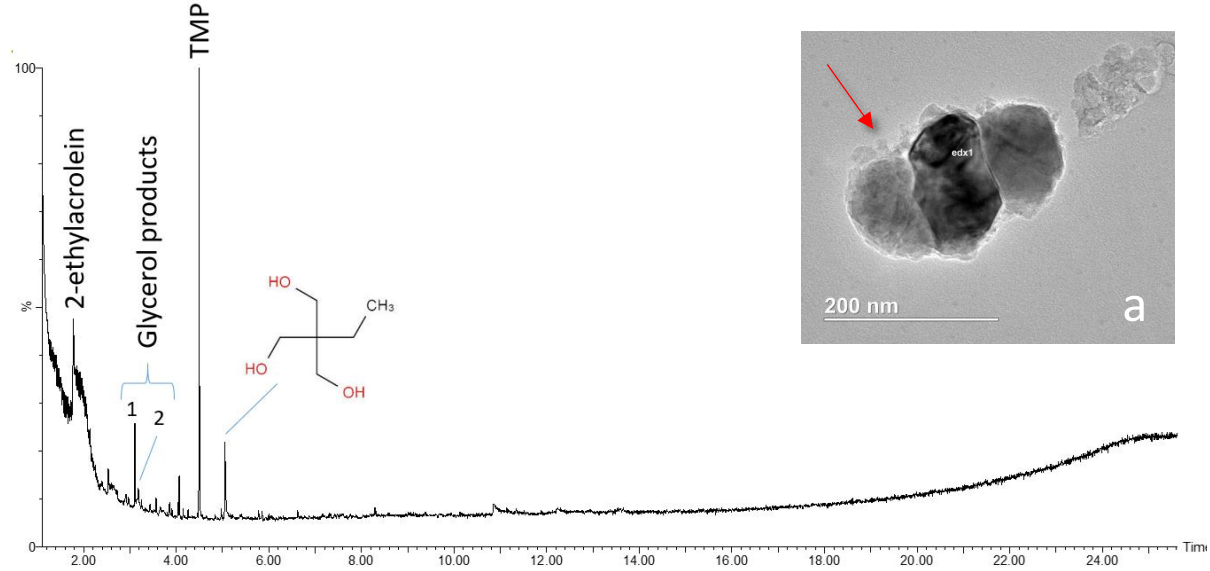


Figure 18. GCMS trace of A3 with TMAH showing peaks related to 2-ethylacrolein, and Glycerol products (1: Propane, 1,2,3, trimethoxy and 2: Diethylene glycol dimethyl ester), and a high dominant peak which was identified as Trimethylolpropane (TMP). Insert: (S)TEM-EDX spectral image of A3- the inorganic coating (Zr, Al) is non-homogeneous, with some loose (coating) material (upper right). Results from Brenda Rossenar (AKZO NOBEL CHEMICALS).

Other significant findings with these techniques were the presence of an antioxidant, Phenol, 2, 4-bis(1,1-dimethylethyl), and a phthalate, 1,2-dimethyl phthalate, in the R2 pigment (see below figure 19).

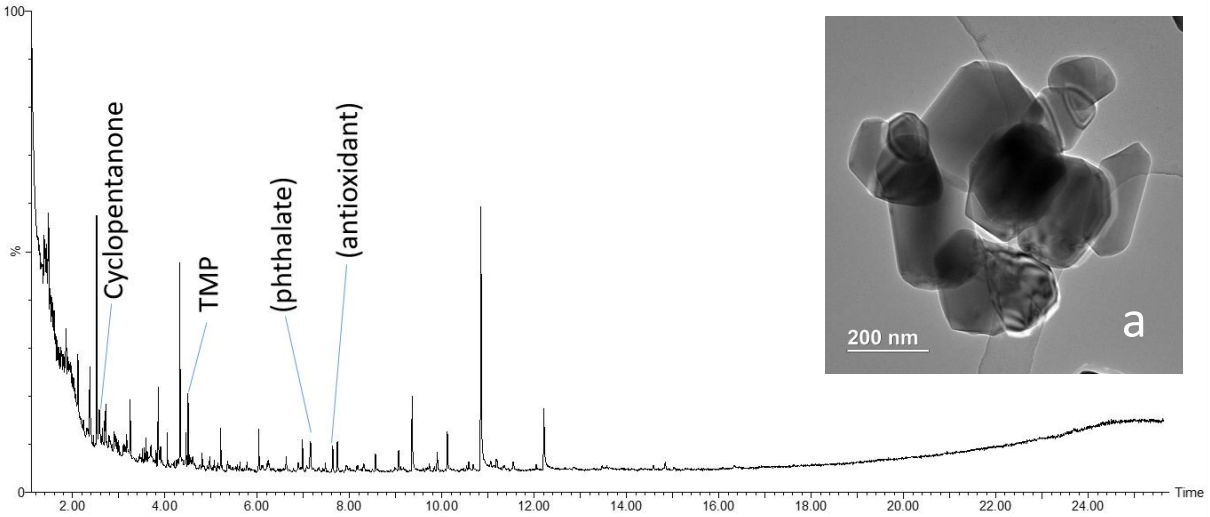


Figure 19. GCMS trace of R2 with TMAH where it can be seen identified Cyclopentanone, a small peak attributed to Trimethylolpropane (TMP), 1,2-dimethyl phthalate (phthalate), and Phenol, 2, 4-bis(1,1-dimethylethyl) (antioxidant). Insert: (S)TEM-EDX spectral image of R2. There is no surface coating visible in the TEM image: either not there or very thin. Results from Brenda Rossenar (AKZO NOBEL CHEMICALS).

Regarding the presence of the anti-oxidant, this can be connected to the fact that R2 is a multifunctional pigment and the manufacturer may add substances preventively to help users [70]. The use of phthalates in pigment surface treaments is common, appearing as grinding aid (see text 1.4.3).

To note that the data-sheet for A2 and A3, both pigments from Huntsman, states that the pigments are “organically treated to promote dispersion in aqueous and non-aqueous systems” [71, 72]. At this date, it is unclear what type of treatment could be used that could function in both systems while being effective for all the end uses that the manufacturer proposes. Also, it is interesting to note that R3, acquired from an artist oil paint manufacturer, was treated with Al and Zr, which as seen above (see text 1.4.3), is a treatment applied for improved durability [43].

To note, that the use of a rutile form over an anatase may also suggest a choice: e.g. durability over whiteness (anatase pigments provide a bluish tone and the rutile is more yellowish) (see text 1.4.3).

Conclusions

The investigation of pigment surface treatments and coatings revealed that these treatments appear in response to industrial uses and needs and are not specifically intended for artist's oil paint manufacturers. Although requirements can be overlapping for the different industries, as Laver (1977) notes, pigment treatments can have unexpected and unwanted behaviour when used in a binder for which they were not originally created [57].

Starting the investigation from a literature search identifying possible treatments and coatings established the importance of gathering information on the pigment's provenance and material characterization. The importance of knowing where and for what purpose pigments are produced should be highlighted, since the investigation of what treatments can be applied may be extrapolated to what type of treatment could be present.

During the literature search it was also found that materials known to have been used as additives for paints were also used as surface treatments for pigments. Early examples are the use of stearates and waxes.

Terminology was another issue. Surface treatments are indeed well-kept secrets. However, as was seen with the TiO_2 pigments, when marked as "uncoated" the manufacturer meant that no inorganic coating was present. This distinction is relevant because, as we have seen, treatments are very complex and can include an organic component (even if only as a grinding aid). Therefore it became evident that where the manufacturer's literature reports that a pigment is "uncoated" this does not necessarily mean that the pigment has not been treated.

Regarding the detection and identification of inorganic treatments: both FEG-SEM and (S)TEM-EDX proved to be effective for this purpose. In addition, by enabling a high resolution magnified view of particle topography, size and shape, these methods also provided evidence which shed light on the method of manufacture of the pigments

Analysis of the organic fraction present in the pigment samples proved to be challenging. Although in this investigation EGA-MS results were inconclusive, and not providing evidence of surface treatments, the pyrolysis methods did enabled the identification of anticipated materials (as was the case of the polyols) as well as the discovery of unexpected compounds such as anti-oxidants.

For future research, since it is not currently understood whether these surface treatments may affect the paint system, further investigation should be conducted. As Schröder (1988) states "a wealth of (…) knowledge exists in the safes of many pigment manufacturers and other companies" [4, p. 5]. Therefore, for future work, partnerships with companies that own relevant archives should be established in order to investigate and achieve a more detailed understanding of the practical application of these treatments and how they can influence artist's oil paints. The existence of a visual dictionary would also be a complementary tool of a great help to identify coatings and understand how different materials and methods of application look (e.g. rosin coating vs gold coating, vs silica coating.). Such dictionary could be done developed following a selective approach, addressing step by step sets of coatings which share, for instance, common morphology and known application methods.

References

[1] Ball, Phillip. 2001. *Bright Earth: the Invention of Colour*. London: Vintage Books.

[2] De Keijzer, Matthijs. 2002. "The history of modern synthetic inorganic and organic artists' pigments". In *Contributions to conservation: research in conservation at the Netherlands Institute for Cultural Heritage (ICN Instituut Collectie Nederland)*, edited by Jaap A. Mosk and Norman H. Tennent, 42-54. London (UK): James & James.

[3] Lenoir, J. 1971. "Organic Pigments". In *The Chemistry of Synthetic Dyes,* Vol. 5, edited by Krishnasami Venkataraman. New York: Academic Press.

[4] Schröder, Jörg. 1988. "Surface Treatment of pigments". Progress in organic pigments. 16: 3-17.

[5] Carr, W. 1973. "Improving the Physical Properties of Pigments: Pigment Elaborations". In *Characterization and Physical Relationships. Vol 3 of Pigment Handbook*, edited by Temple C. Patton, 29-35. New York: Wiley.

[6] Carlyle, Leslie. 2018. "Towards historical accuracy in the production of historic recipe reconstructions" Tempera 2018 Conference, Doerner Institut, Munich, Germany, postprints in press http://www.doernerinstitut.de/tempera_2018/

[7] Carlyle, Leslie. 2012."Chapter 2: Exploring the Grammar of Oil Paint through the Use of Historically Accurate Reconstructions". In *The Conservation of Easel Paintings*, edited by Joyce Hill Stoner and Rebecca Anne Rushfield, 33-38. Abingdon, Oxon (UK): Routledge.

[8] ConferenceMOP abstract book 2018

[9] Keune, Katrin and Jaap Boon. 2007. "Analytical Imaging Studies of Cross-Sections of Paintings Affected by Lead Soap Aggregate Formation". *Studies in Conservation*. 52(3):161-176

[10] Osmond, Gillian. 2014. "Zinc oxide-centred deterioration of modern artist's oil paint and implications for the conservation of twentieth century paintings". PhD diss., University of Queensland Australia.

[11] van Driel, Birgit. 2018. "Titanium White, Friend or Foe?: Understanding and predicting photocatalytic degradation of modern oil paintings". PhD diss., Delft University of Technology.

[12] Barnett, C. E. 1949. "Physics and Chemistry of pigments". *Industrial and Engineering Chemistry*.

[13] Fisher, E. K. 1950. "Surface-active agents". In *Colloidal Dispersions*, John Wiley & Sons, New York, pp. 224-257

[14] Merkle, K and F. Shäffer. 1973. "Surface treatment of organic pigments". In *Characterization and Physical Relationships. Vol. 3 of Pigment Handbook*, edited by Temple C. Patton, New York: Wiley.

[15] Hays, B. G. 1984. "Surface Treatment of Organic Pigments for Printing". American Inkmaker 62(6):28-50.

[16] Bugnon, Phillipe. 1996. "Surface Treatment of Pigments: Treatment with inorganic materials". Progress in Organic Pigments. 29(1-4):39-43.

[17] Brundle, R., Charles A. E. Jr. and Shaun W. 1992. *Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films*. United States of America.

[18] N. Erdman, N. Kikuchi, A. Laudate and V. Robertson. 2009. Multispectral imaging in an FEG-SEM. Advanced Materials & Processes [accessed 10 September 2018]. Available at: https://www.jeolusa.com/DesktopModules/Bring2mind/DMX/Download.aspx?EntryId=610&Command=Core_Download&language=en-US&PortalId=2&TabId=320-

[19] Egerton, T. A. 1998. "The modification of Fine Powders by Inorganic Coatings". *KONA*. 16: 46-59.

[20] Hutton, R. C. 1984. "The Analysis of Surface Coatings and Raw Materials. Techniques used in the analysis of titanium(IV) oxide pigments". *Analytical Proceedings*. 21:317-319

[21] Tsuge, Shin, Hajima Ohtani and Chuichi Watanabe. 2018. *Pyrolysis - GC/MS Data Book of Synthetic Polymers: Pyrograms, Thermograms and MS of Pyrolyzates*

[22] Carlyle, L. 2000. Molart Fellowship – Historical Reconstructions of Artist's Oil Paint: an investigation of oil processing methods and the use of medium-modifiers. Canadian Conservation Institute

[23] Golden, Mark. Fall 2016. "Manufacturing Artists Paints: Keeping Pace with Change". *Conservation Perspectives: The GCI Newsletter*, 31(2):16-18. http://www.getty.edu/conservation/publications_resources/newsletters/pdf/v31n2.pdf

[24] Ferreira, Cátia Beatriz. 2018 (unpublished). “Investigating surface treatments and coatings, their history, application and detection on selected pigments: Umber, Vine Black, Ultramarine Blue, Cu-Phthalocyanine Blue, and two Hansa Yellows, PY3 and PY74”. Ms Thesis, Universidade NOVA de Lisboa, Faculdade de Ciências e Tecnologia

[25] Wicks, Z. W., F. N. Jones, S. P. Pappas, and D. A. Wick., eds. 2017. “Pigments”. In *Organic Coatings: Science and Technology*, 4th ed., 293–434. New Jersey: John Wiley & Sons

[26] Levison, Henry W. 1973. “Pigmentation of Artist’s Colors”. In *Applications and Markets. Vol 3 of Pigment Handbook*, edited by Temple C. Patton, 423-434. New York: Wiley

[27] Senna, M .2006. “Surface Modification. In *Powder Technology: Fundamentals of Particles, powder beds, and particle*, edited by Yoshida H, Masuda H, Higashitani K , 3rd ed. CRCPress, Boca Raton, pp. 485-491

[28] Herbst, Willy, Klaus Hunger, Gerhard Wilkner. 2004. *Industrial Organic Pigments: Production, Properties, Applications,* 3rd edition. Weinheim : Wiley-VCH.

[29] Chavda, Vivek P, Moinuddin M. Soniwala and Jayant R. Chavda. 2013. “Particle coating: From conventional to advanced”. *International Journal of Pharmaceutical and Medicinal Research.* 1:1-17.

[30] Clarke, Marke. 2011. *Mediaeval Painters: Materials and Techniques: The Montpellier ‘Liber diversarum arcium*. London: Archetype Publications

[31] Johnston, Henry M. 1870. Improvements in pigments for Distemper Paints. US Patent 99,907, filed February 15, 1870.

[32] Coolidge, Cole and Harold S. Holt. 1932. Noncaking pigment. US Patent 2,009,436, filed May 24, 1932.

[33] Gardner, Henry A. 1933. Process of modifying the characteristic of pigments and product. US Patent 1,894,168, filed Jan 22, 1931.

[34] Meister, F Walter and N. J. Elizabeth.1938. Pigments of improved wetting, dispersing, and nonsettling characteristics and the process of manufacturing same. US Patent 2,133,539, filed June 7, 1933.

[35] 0’Brien, William J. 1937. Process of coating pigments. US Patent 2,068,066, filed June 14, 1932.

[36] Izzo, Francesca Caterina, Klaas Jan van den Berg, Henk van Keulen, Barbara Ferriani, and Elisabetta Zendri. 2014. Modern Oil Pints – Formulations, Organic Additives and Degradation: some case studies. In *Issues in Contemporary Oil Paint*, edited by K. J. van den Berg, A. Burnstock, M. Keijzer, A. Teagle, and G. Heydenreich, 75-104. Cham: Springer.

[37] Stesikova, Elvira and Heinz Plaumann. 2012. “Surfactants”. In *Paint and Coating Testing Manual: Fifteenth Edition of the Gardner-Sward Handbook 15th Edition*, edited by Joseph V. Koleske, 320-331. Bridgeport, NJ: ASTM International.

[38] Oyarzún, J. 1999. “Physical characterization of pigments”. In *Pigment Processing: Physico-Chemical Principles*, edited by Ulrich Zorll, 13-20. Hannover: Vincentz.

[39] Lu, Shouci, Robert J. Pugh, and Eric Fossberg. 2005. “Chapter 3: Modification of particle surfaces”. In Interfacial Separation of Particles, 97-172. Amsterdam: Elsevier p. 5

[40] Vernardakis, T. 2007. “Chapter 31 - Pigment Dispersion”. In *Coating Materials and Surface Coatings*, edited by Arthur A. Tracton, 1-19. California: CRC Press.

[41] Pfaff, Gerhard. 2017. *Inorganic Pigments*. Berlin: Walter de Gruyter GmbH.

[42] Buxbaum, Gunter and Gerard Pfaff, eds. 2005*. Industrial Inorganic Pigments. 3rd ed*. Weinheim: Wiley VCH.

[43] Braun, J. H., Baidins, A., and Marganski, R. E. 1992. “TiO2 pigment technology: a review”. *Progress in Organic Coatings*. 20(2): 105-138.

[44] Abel, A. G. 1999. “Pigments for paint”. In *Paint and Surface Coatings: Theory and Practice*, edited by R. Lambourne and T. Strivens, 2nd ed., 91-165. Cambridge: Woodhead Publishing.

[45] Bieleman, Johan, ed. 2000. Additives for Coatings. Weinheim: Wiley-VCH.

[46] Veronovski, N., M. Lesnik and D. Verhovsek. 2014. “Surface Treatment optimization of pigmentary TiO_2 from an industrial aspect”. *Journal of coating Technology.*

[47] Winckler, Jochen. 2003. *Titanium Dioxide*. Hannover: Vincentz Network.

[48] Farrohkpay, Saeed. 2004. Interaction of Polymeric Dispersants with Titania Pigment Particles. PhD diss., University of South Australia
[49]Schoffield, John. 2002. “Extending the boundaries of dispersant technology*”. Progress in Organic Coatings.*45: 249–257
[50] Napper, Donald. 1983. *Polymeric stabilization of colloidal dispersions.* London*:* Academic Press
[51] Moezzi, Amir, Andrew M. McDonagh and Michael B. Cortie. 2012. “Zinc oxide particles: Synthesis, properties and applications”. *Chemical Engineering Journal.* 185– 186:1– 22
[52] Schofield, John and Pat Suderland. 2007. Application Specific Surface Treatments for Calcium Carbonate Type fillers in high performance systems. In *High Performance Fillers*.
[53] Boon, Jaap J. and Frank G. Hoogland. 2014. “Investigating Fluidizing Dripping Pink Commercial Paint on Van Hemert’s Seven-series Works from 1990-1995” In *Issues in Contemporary Oil Paints*, edited by K. J. van den Berg, A. Burnstock, M. Keijzer, A. Teagle, and G. Heydenreich, 227-246. Cham: Springer.
[55] Gettens, R. J., H. Kühn, and W.T. Chase. 1993. "Lead White". In Vol. 2 of *Artists Pigments*, edited by A. Roy. Oxford University Press: Oxford.
[56] Eastaugh, Nicholas, Valentine Walsh, Tracey Chaplin and Ruth Siddall. 2008. *Pigment Compendium: A Dictionary and Optical Microscopy of Historical Pigments.*
[57] Laver, Marilyn. 1997.”Titanium Dioxide Whites". In *Artists’ Pigments: A Handbook of Their History and Characteristics*, Vol. 3, edited by Elisabeth West FitzHugh, 295-323. 1977 ed. Oxford: National Gallery of Art
[58] Campos, Marta Félix. 2010. “The Study of Lead White Oil Paints”. Ms Thesis, New University of Lisbon, Faculty of Science and Technology
[59] Gonzalez, Victor, T. Calligaro, G. Wallez, M. Eveno, K. Toussaint and M. Menua. 2016. “Composition and microstructure of the lead white pigment in Masters Paintings using HR Synchrotron XRD”. *Microchemical Journal.* 25: 43-49
[60] Ramage, Alexander S. 1911. Lead Pigment and Method of Making the Same. US Patent 982,992, filed Jan 3, 1910.
[61] Jones, Leo D. 1932. Production and Recovery of Dispersed Substances. US Patent 1,854,744, filed November 27, 1925.
[62] Moilliet, J. and D. Plant. 1969. “Surface treatment of pigments”. *Journal of the Oil and Colour Chemists’ Association*. 52:288-308.
[64] Haslam, George S. 1938. Rubber compounding. US Patent 2127560A, filed August 23, 1938.
[63] Craig, Daniel H. 2006. Surface-treated pigments.US Patent 0042512 A1, filed August 30, 2004.
[65] Depew, Harlan A. 1942. Nonreactive Pigment. US Patent 2,277,393, filed May 29, 1939.
[66] Carlyle, Leslie. 2001. *The Artist’s Assistant – Oil Painting Introduction Manuals and Handbooks in Britain 1800-1900 With References to Selected Eighteenth-century Sources*. London: England.
[67] Capelle, Hendrick A. 2006. “Titania Pigment Surface Modification for improved Plastic Dispersion”. PhD diss., University of South Australia.
[68] Iler, Ralph K. 1959. Product comprising a skin of dense, hydrated amorphous silica bound upon a core of another solid material and process of making same. US Patent 2,885,366, filled June 28.
[69] Huntsman safety data-sheet. 2008. http://www.ucgen.com.tr/Web_Data/Contents/UCGEN/Media/tds-msds/Huntsman/MSDS/Europe-Generic-GB-DELT-O81X-2008-01.pdf.
[70] Huntsman HDCD safety data-sheet. http://www.ucgen.com.tr/Web_Data/Contents/UCGEN/Media/tds-msds/Huntsman/MSDS/Europe-Generic-GB-DELT-O81X-2008-01.pdf
[71] Huntsman APP2. http://www.ucgen.com.tr/Web_Data/Contents/UCGEN/Media/tds-msds/Huntsman/MSDS/Europe-Generic-GB-DELT-O81X-2008-01.pdf
[72] Huntsman Tioxide A-HRF. http://www.maydi.si/files/Huntsman_titanovoksid_anatas.pdf

UNITED STATES PATENT OFFICE.

HENRY M. JOHNSTON, OF NEW YORK, N. Y.

IMPROVEMENT IN PIGMENTS FOR DISTEMPER PAINTING.

Specification forming part of Letters Patent No. 99,907, *dated February* 15, 1870.

Now it is the object of my invention to supply dry pulverized pigments of all desired colors, having the binding or adhesive materials intimately incorporated with the pigments, so that it will only be required to mix them with a stated quantity of water to render them fit for use.

I will now proceed to describe the methods I prefer for producing dry, pulverized, sized; or adhesive pigments, which will enable others skilled in the art to fully understand and make use of the same.

following manner:

I take a given quantity of any of the pigments that may be required to produce the color desired and grind them to a fine powder, after which I make use of any suitable adhesive substance that is soluble in water and that is fitted to bind the pigments used, and I reduce it to a fine pulverized condition by grinding in a mill or in any other suitable manner. I then add the requisite quantity of pulverized adhesive substance to the powdered pigments and thoroughly incorporate

Figure 6. US Patent by Johnston, dated 1870, proposing the use of "adhesive substances" soluble in water for the surface treatment of pigments [31].

UNITED STATES PATENT OFFICE

2,009,436

NONCAKING PIGMENT

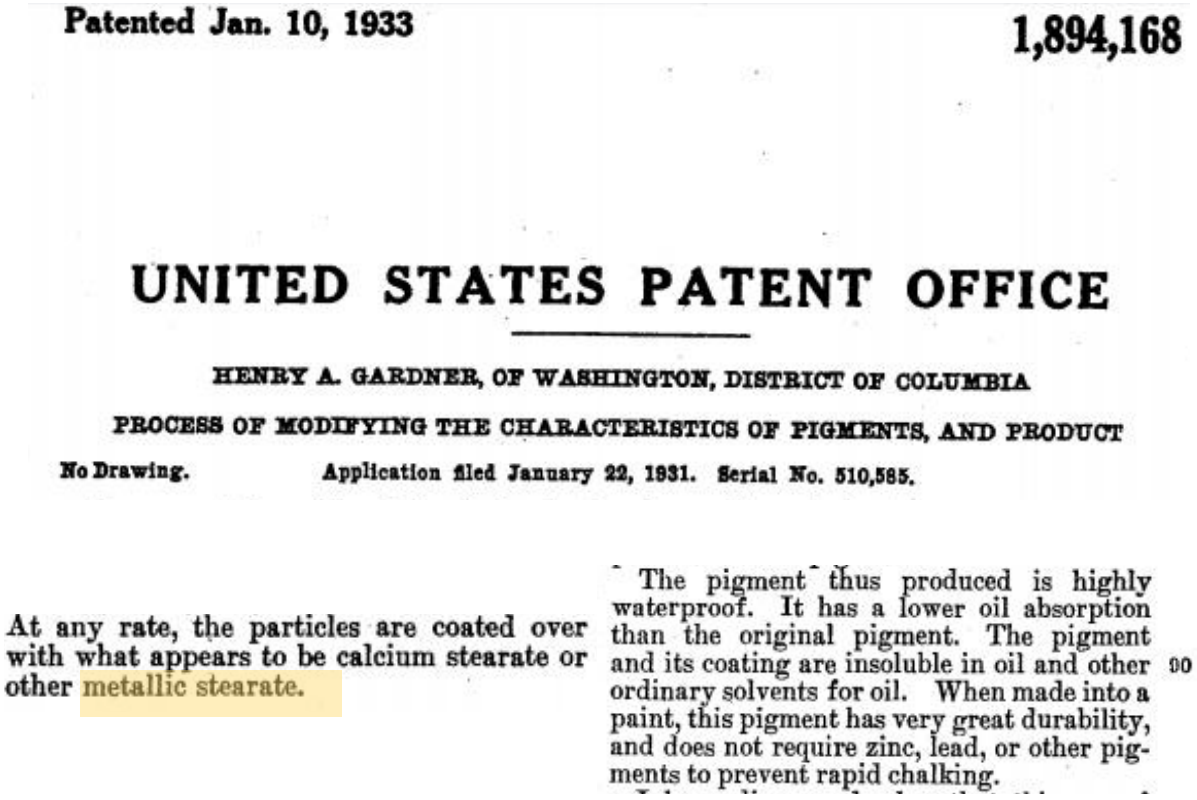
Cole Coolidge and Harold S. Holt, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application May 24, 1932, Serial No. 613,262

6 Claims. (Cl. 134—58)

As regards the protective agent itself, we may employ in addition to those cited, a large number of others as follows: spermaceti, candelilla wax, crude Montan wax, beeswax, laurel wax, sugar cane wax, gondang wax, pisang wax, palm wax, raphia wax, rhimba wax, psylla wax, a variety of stearin pitches, and a number of synthetic ester-waxes such as lauryl stearate, cetyl palmitate, waxes obtained by the hydrogenation of fats and oils, and waxes obtained from aldehydes by aldol condensation, reduction, and esterification.

Figure 7. US Patent by Coolidge, Cole and Harold S. Holt., dated 1932, proposing the use of waxes for the surface treatment of pigments [31].



Patented Jan. 10, 1933 1,894,168

UNITED STATES PATENT OFFICE

HENRY A. GARDNER, OF WASHINGTON, DISTRICT OF COLUMBIA

PROCESS OF MODIFYING THE CHARACTERISTICS OF PIGMENTS, AND PRODUCT

No Drawing. Application filed January 22, 1931. Serial No. 510,585.

At any rate, the particles are coated over with what appears to be calcium stearate or other metallic stearate.

The pigment thus produced is highly waterproof. It has a lower oil absorption than the original pigment. The pigment and its coating are insoluble in oil and other ordinary solvents for oil. When made into a paint, this pigment has very great durability, and does not require zinc, lead, or other pigments to prevent rapid chalking.

Figure 8. US Patent by Gardner, dated 1933, proposing the use of metallic stearates for the surface treatment of pigments [32].

2.1. Materials

All reagents used were of analytical grade. Tetramethylammoniym hydroxide (TMAH) was used for Py-THM-GC/MS analysis. Electron Microscopic studies on pigment powders were carried out on aluminium stubs covered with copper tape. Mass Spectrometry studies were carried out in eco-cups SF®, from Frontier Lab. Sample Preparation.

2.2. Instruments and methods

2.2.1 Sample preparation

SEM-EDX

In an aluminium stub with copper tape, the smallest amount of sample possible was deposited on the stub surface under a stereomicroscope with the aid of a metallic spatula; excess pigment powder was blown off with air.

FEG-SEM

Samples were the same as those used for SEM-EDX.

TEM-EDX

Electron transparent films for STEM-EDX were prepared with a Leica UC7 Ultramicrotome. Pigment particles were mixed in purified H_2O and frozen at -80 in the cryochamber of the Ultramicrotome.
TEM slices were prepared with a cryo 35 diamond knife with a cutting speed of 1 mm/sec and a feed of 70 nm; Sections were collected dry using the charge/discharge function on 200 mesh C filmed Cu grids and holycarbon filmed Cu grids.

EGA-MS

Micro-samples of pigment were placed into a stainless steel cup (Frontier Disposable Eco-Cup LF). Pigment particles were observed under microscope and agglomerates were broken down. The procedure was repeated with the slightest increase in the amount of pigment sample when the results were not significant.

Py-GC/MS

Same procedure as EGA-MS.

Py-THM-GC/MS

With a dissecting needle 0.05 µL of tetramethylammonium hydroxide (25 % in methanol) is applied to a small vial with the smallest amount possible of pigment sample. The solution is homogeneized, a dissecting needle is dipped in the solution of pigment/TMAH and a drop is deposited in a stainless steel cup (Frontier Disposable Eco-Cup LF). The procedure is repeated with the slightest increase in the amount of pigment sample when the results were not significant.

2.2.2. Apparatus

SEM-EDX

The Scanning electron microscope (SEM) used was a JEOL JSM-5910 with secondary (SE) and backscattering (BSE) detectors coupled to an energy dispersive X-ray spectrometer (EDS). The analyses were carried out under low vacuum conditions where the samples did not have charging effects; The spectra were acquired with a voltage of 15 kV, 10 mm of working distance, spot size 44 and energy of 30Pa. The samples were analysed with Point and Shoot mode. The copper signal in the SEM-EDX spectra is due to the copper tape. Analysis were carried out by Cátia Ferreira at RCE.

(S)TEM-EDX

TEM Bright Field (BF) and STEM-EDX investigations were conducted with a JEOL 2010F TEM operated at 200 kV and equipped with a Thermo Scientific Ultra Dry SDD for EDX analysis; EDX Spectrum Images (SI) were acquired with the Thermo Scientific NSS Software; Principal Component Analysis (PCA) was applied for phase identification in the SI. Analysis were carried out at AKZO NOBEL Chemicals by Brenda Rossenar and Arn Janssen.

FEG-SEM

All analysis were performed by Ineke Joosten, conservation scientist at the RCE. The Field Emission Gun Scanning Electron Microscope (FEG-SEM) used was Nova Nano SEM450 from FEI, with backscattering (BSE) and concentric (insertable) higher energy electron (CBS) detectors. The analyses were carried out under high vacuum conditions; The spectra were acquired with a voltage of 2 kV and 6,3 mm of working distance. Analysis were carried out at RCE by Ineke Joonsten.

Py-GC/MS

Selected samples were analysed using thermally assisted hydrolysis and methylation (THM) gas chromatography-mass spectrometry (GC/MS) in combination with ultrafast thermal desorption (UTD) (see 3.1, 3.2 and 3,3).

For the THM-UTD-GC/MS analyses sample material was made into a suspension with a few drops of a 5% solution of tetramethylammonium hydroxide (TMAH) in methanol with tridecanoic acid (FA-C13) internal standard and the suspension was transferred to a steel pyrolysis cup. The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Trace 1310 GC / ISQ mass spectrometer combination. Ultrafast thermal desorption was performed by heating at 500°C/min from 360°C up to 700°C. The analytical column was directly coupled to the pyrolyser via a home-made split device. A SLB5 ms (Supelco) column was used (length 20 m, int. diameter 0.18 mm, film thickness 0.18 µm). Helium was used as carrier with a constant flow of 0.9 ml/min and split ratio of 1:30. The temperature program was the following: 35 °C (1.5 min), heating at 60 °C /min to 100 °C, heating at 14 °C/min to 250 °C, heating at 6 °C/min to 315 °C (1.5 min). The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 270 °C, the temperature of the ion source was 220 °C. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1, AMDIS 2.7 and MassLynx 4.0 software were used for collecting and processing of the data.

EGA-MS

The samples were analysed using EGA-MS. The samples were directly introduced into a steel pyrolysis cup. The pyrolysis unit used was a Frontier Lab 3030D pyrolyser mounted on a Thermo Scientific Trace 1310 GC / ISQ mass spectrometer combination. EGA was performed by heating at 70°C/min from 70°C up to 700°C. The analytical column was directly coupled to the pyrolyser via a home-made split device. A short deactivated, uncoated capillary (length 1 m, int. diameter 0.1 mm) connects the pyrolyser to the mass spectrometer. Helium was used as carrier with a constant flow of 0.9 ml/min and split ratio of 1:20. The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 270 °C, the temperature of the ion source was 220 °C. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1, AMDIS 2.7 and MassLynx 4.0 software were used for collecting and processing of the data

3.1. SEM-EDX analysis of Lead White pigments

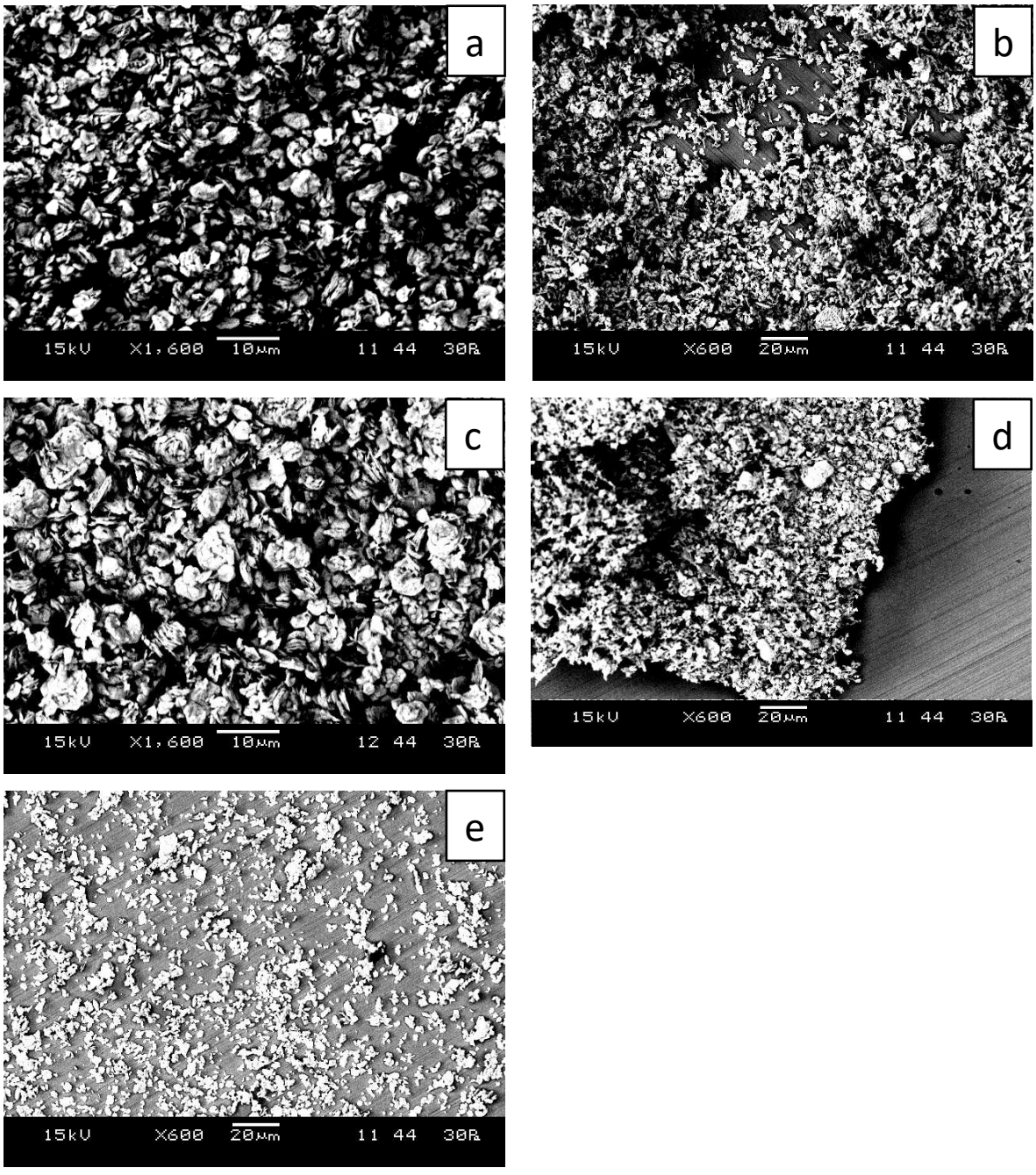


Figure 9. SEM-EDX images of Lead White acquired in LV mode, showing the visual appearance of a) a) 8233, b) 9612, c) 9641, d) Kremer and e) Schoonhoven, SEM-EDX images were acquired by Cátia Ferreira

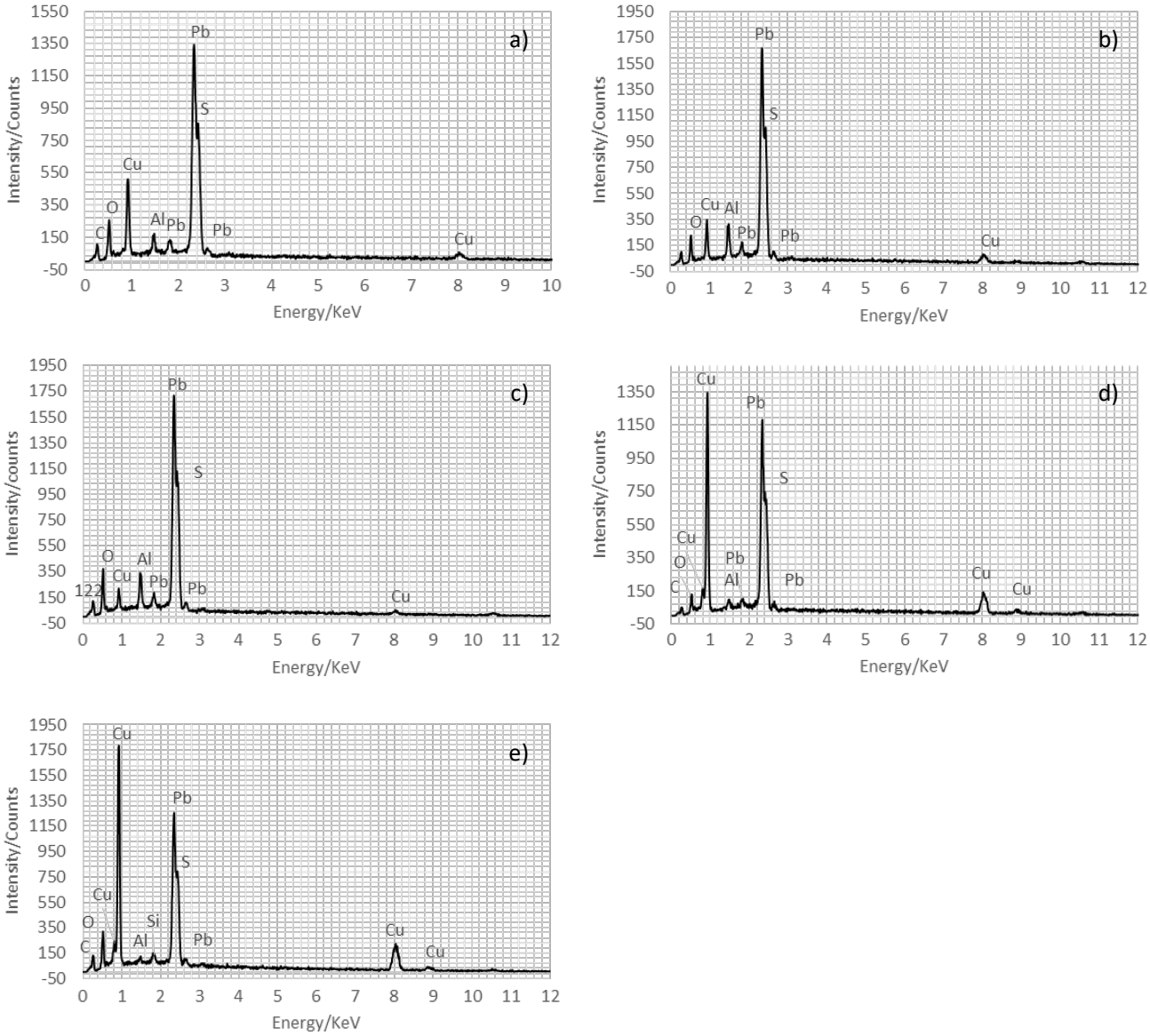


Figure 10. SEM-EDX spectra of Lead White pigments a) 8233, b) 9612, c) 9641, d) Kremer and e) Schoonhoven, at 15 kV. Cu signal is attributed to the copper tape. SEM-EDX spectra were acquired by Cátia Ferreira

3.2. SEM-EDX analysis of Zinc White pigments

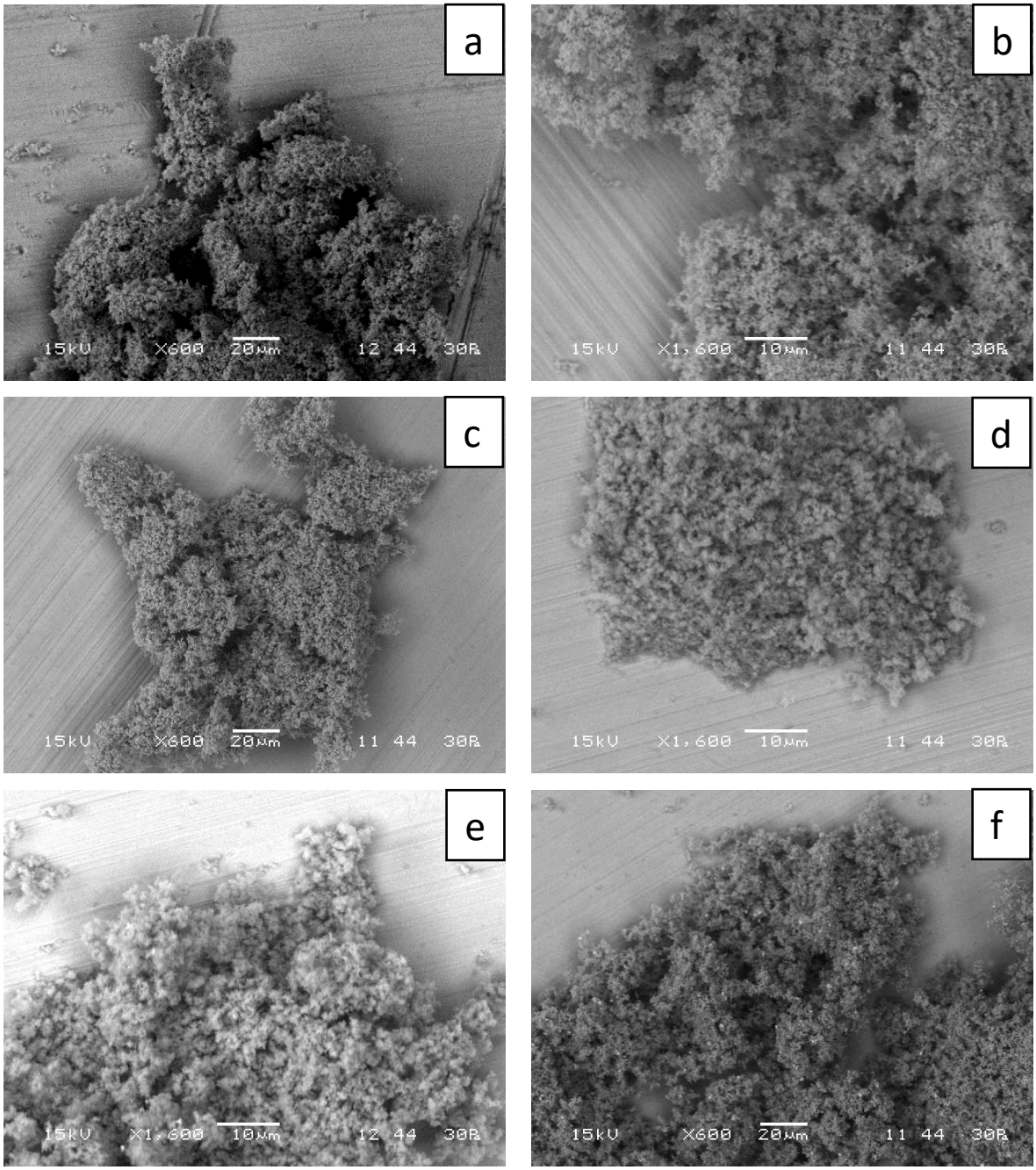


Figure 11. SEM-EDX images of Zinc White pigments acquired in LV mode of a) Carlyle, b) 0191 c) 8232, d) 9496, e) 9647 and f) 9648, SEM-EDX images were acquired by Cátia Ferreira.

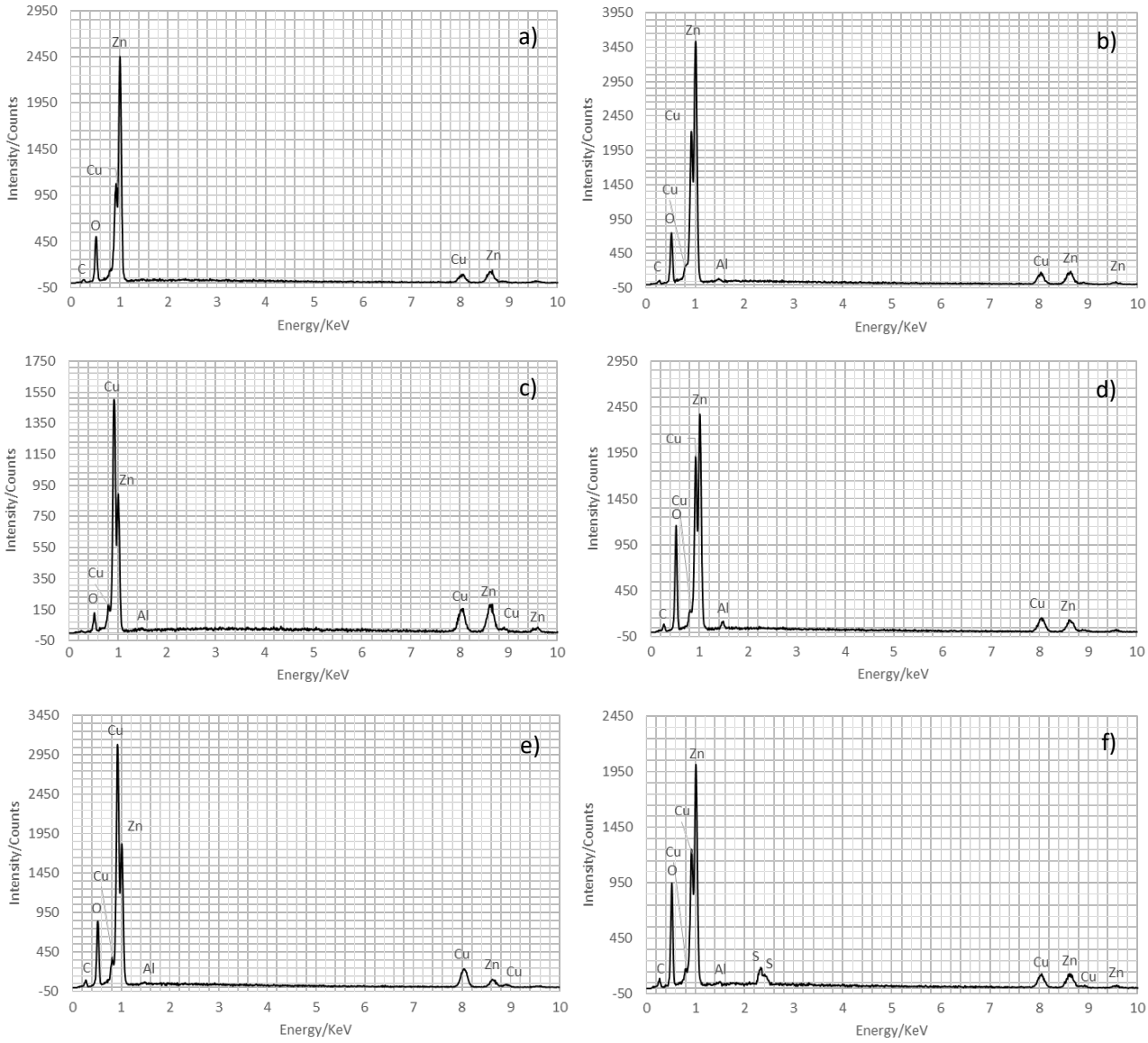


Figure 12. SEM-EDX spectra of Zinc White pigments a) Carlyle, b) 0191 c) 8232, d) 9496, e) 9647 and f) 9648 at 15 kV, SEM-EDX spectra were acquired by Cátia Ferreira.

3.3. SEM-EDX analysis of Titanium White pigment

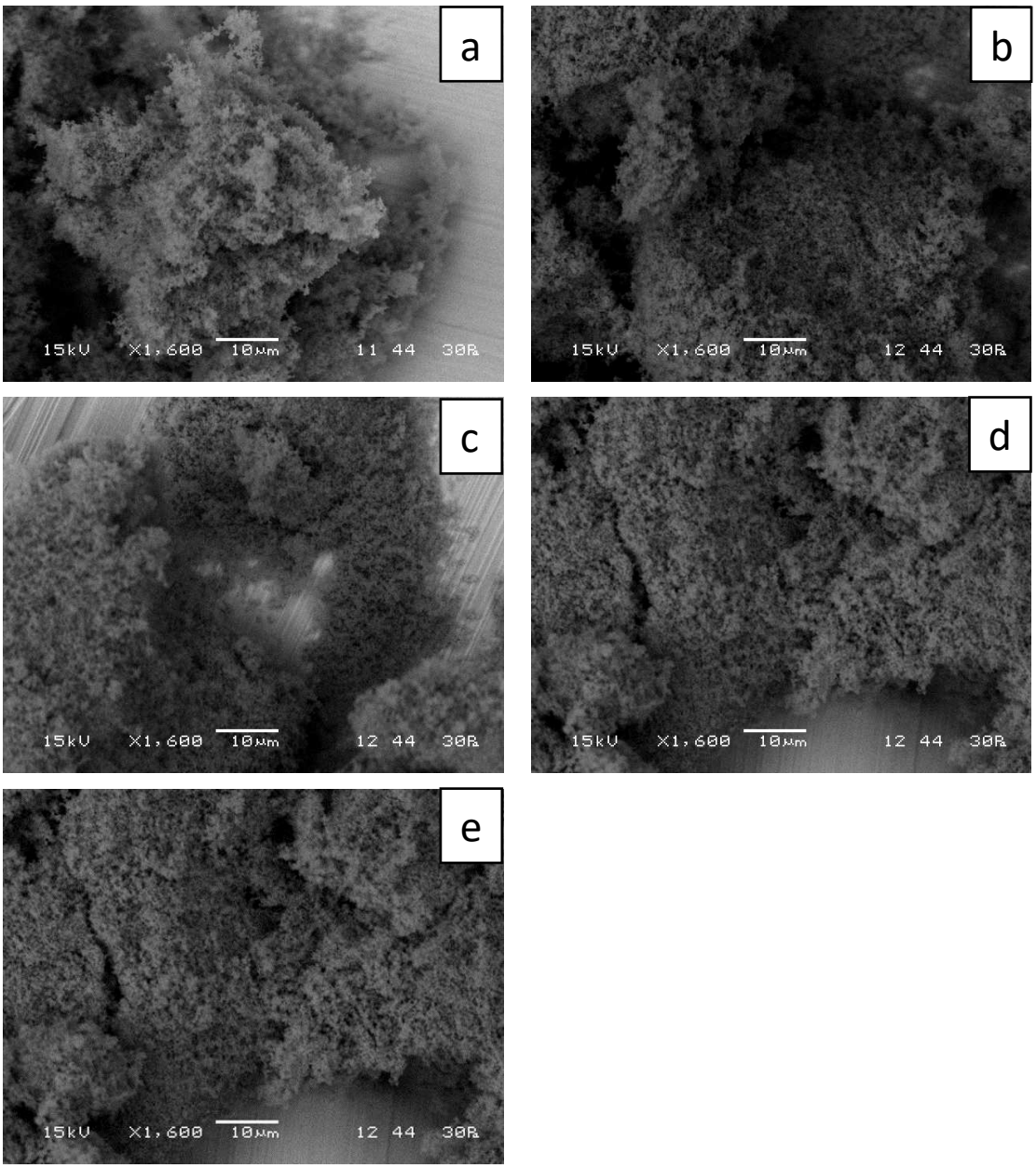


Figure 13. SEM-EDX images of Titanium White pigments acquired in LV mode of a) A1, b) A2 c) A3, d) R2 and e) R3, Cu signal is attributed to the copper tape. SEM-EDX images were acquired by Cátia Ferreira

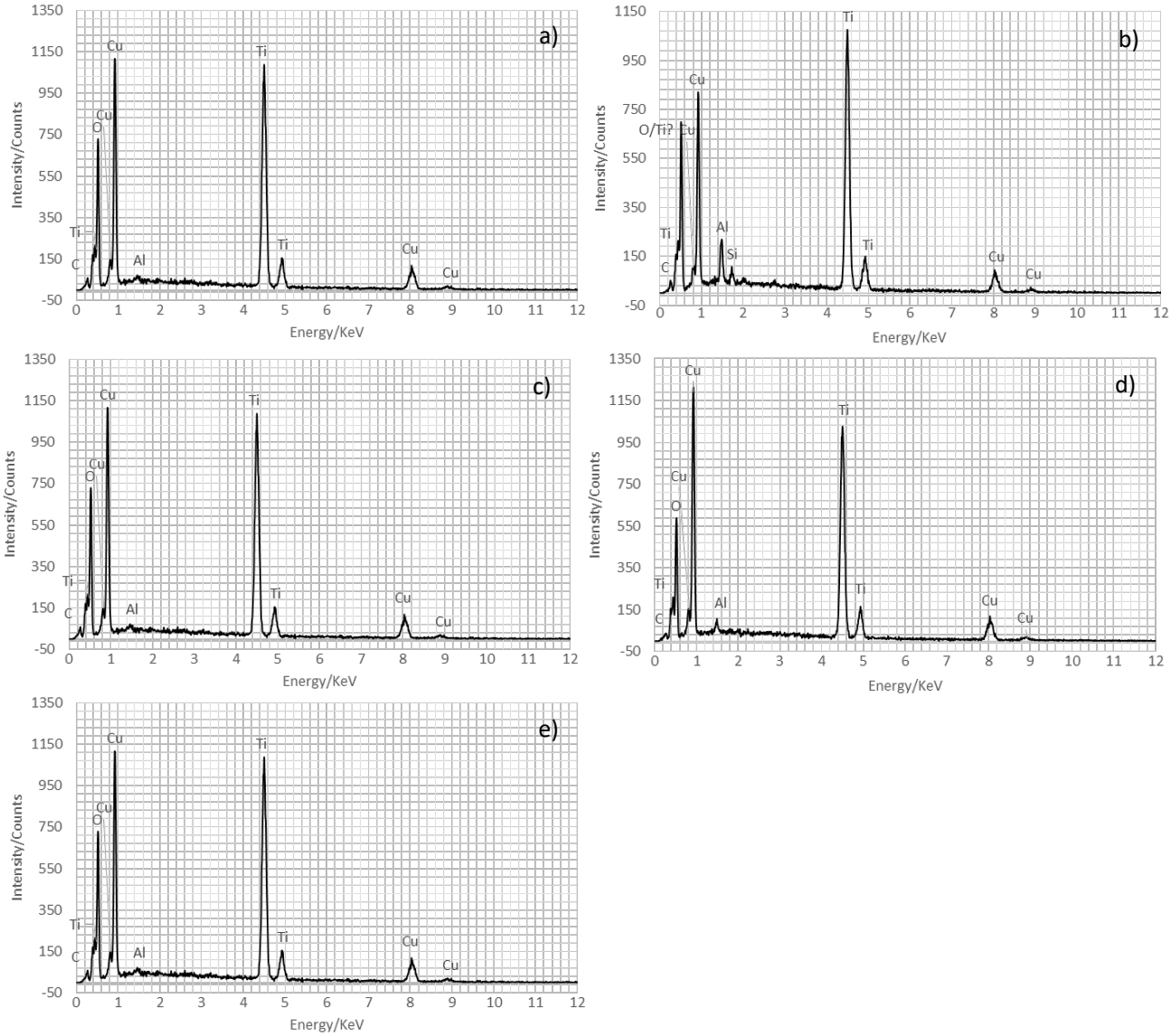
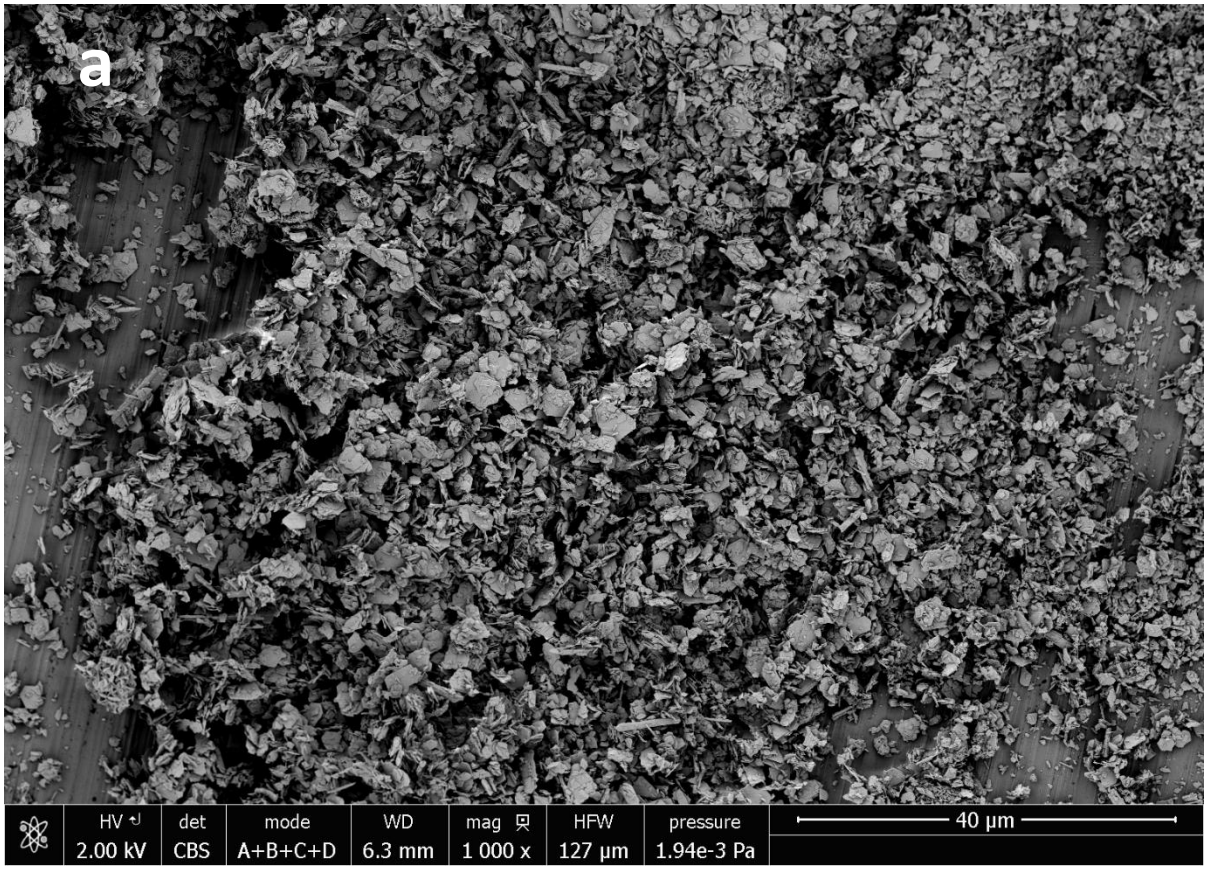


Figure 14. SEM-EDX spectra of Titanium White pigments a) A1, b) A2, c) A3, d) R2 and e) R3, at 15 kV. Cu signal is attributed to the copper tape. SEM-EDX spectra were acquired by Cátia Ferreira.

APPENDIX IV. FEG-SEM analysis

4.1. FEG-SEM Images of Lead White pigments



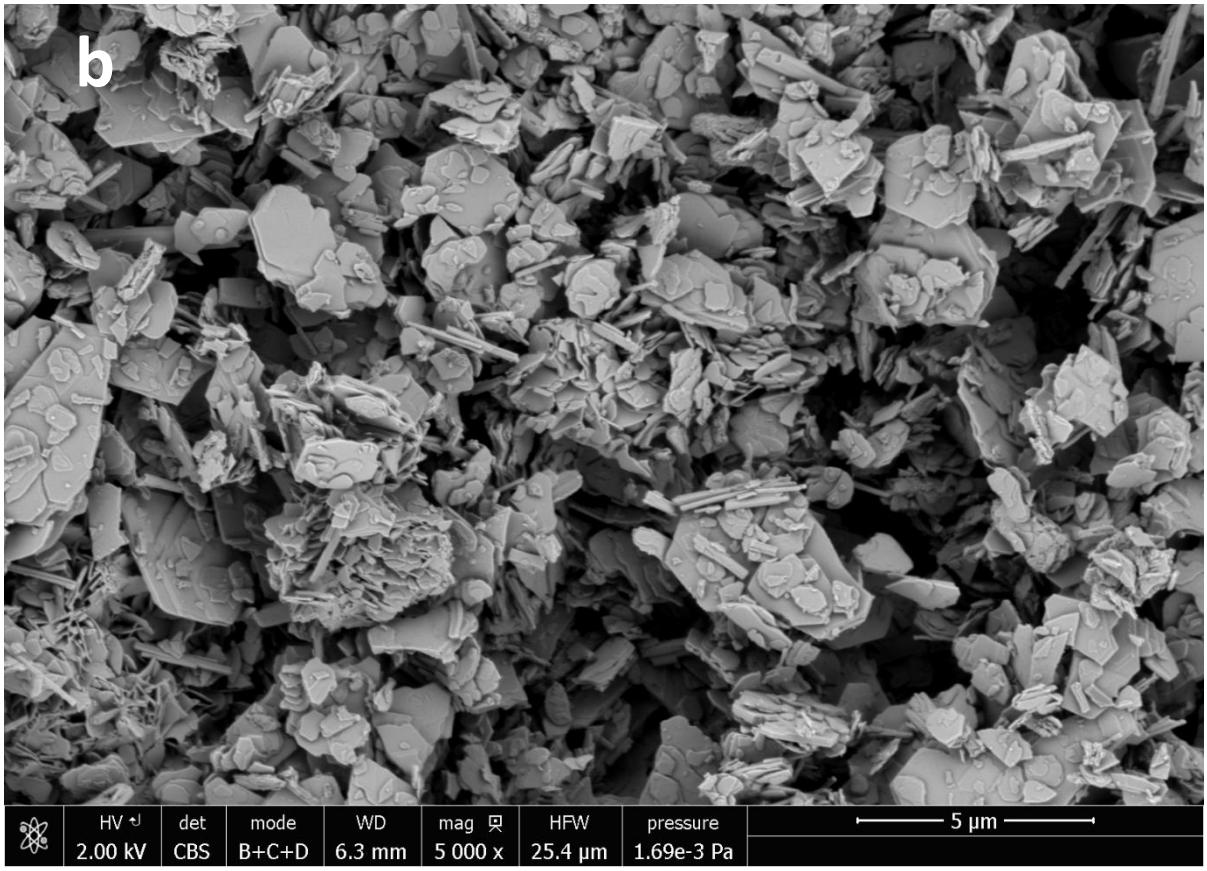


Figure 15. FEG-SEM images in CBS mode showing Lead White Kremer at a) 1.000 x, and b) 5.000 x magnification. Image acquired by Ineke Joosten.

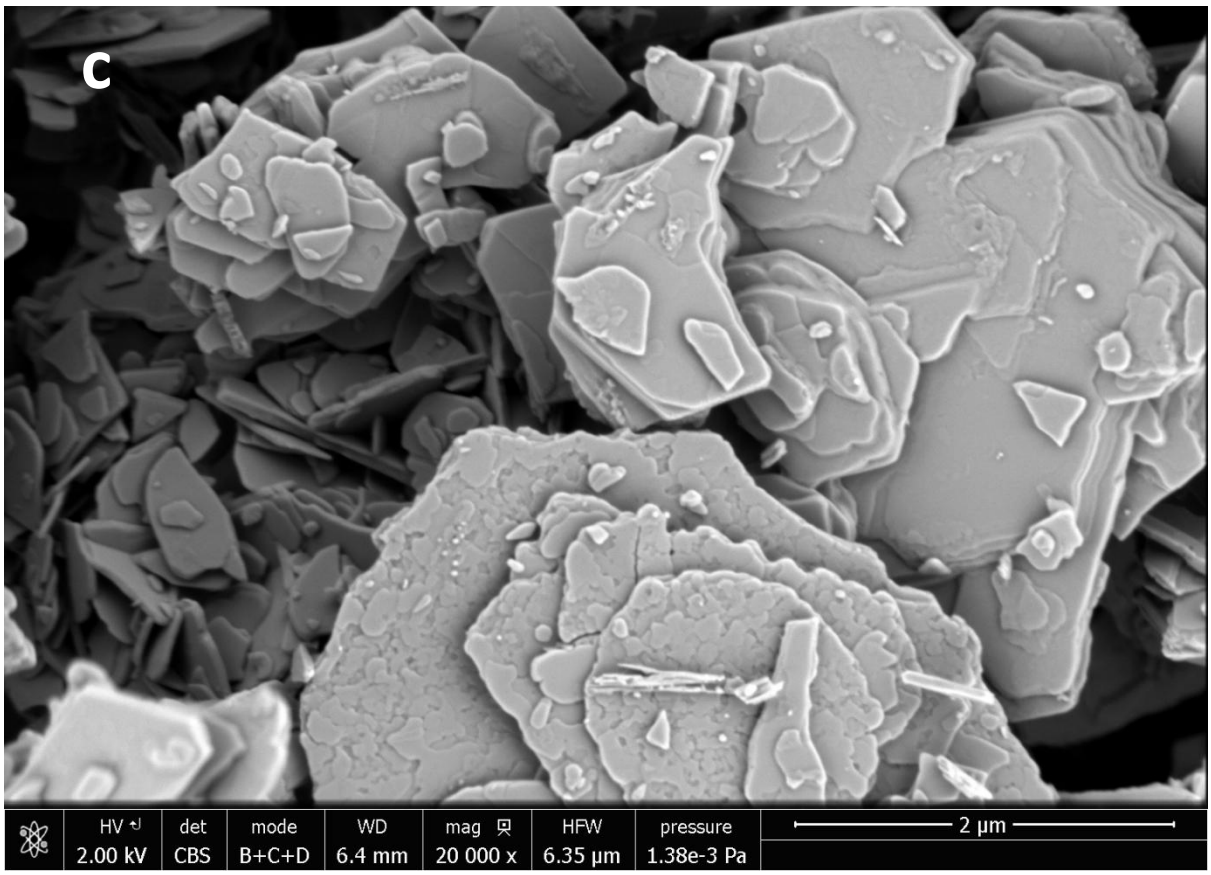


Figure 16. FEG-SEM image in CBS mode showing Lead White Kremer, c) at 20.000 x magnification. Image acquired by Ineke Joosten.

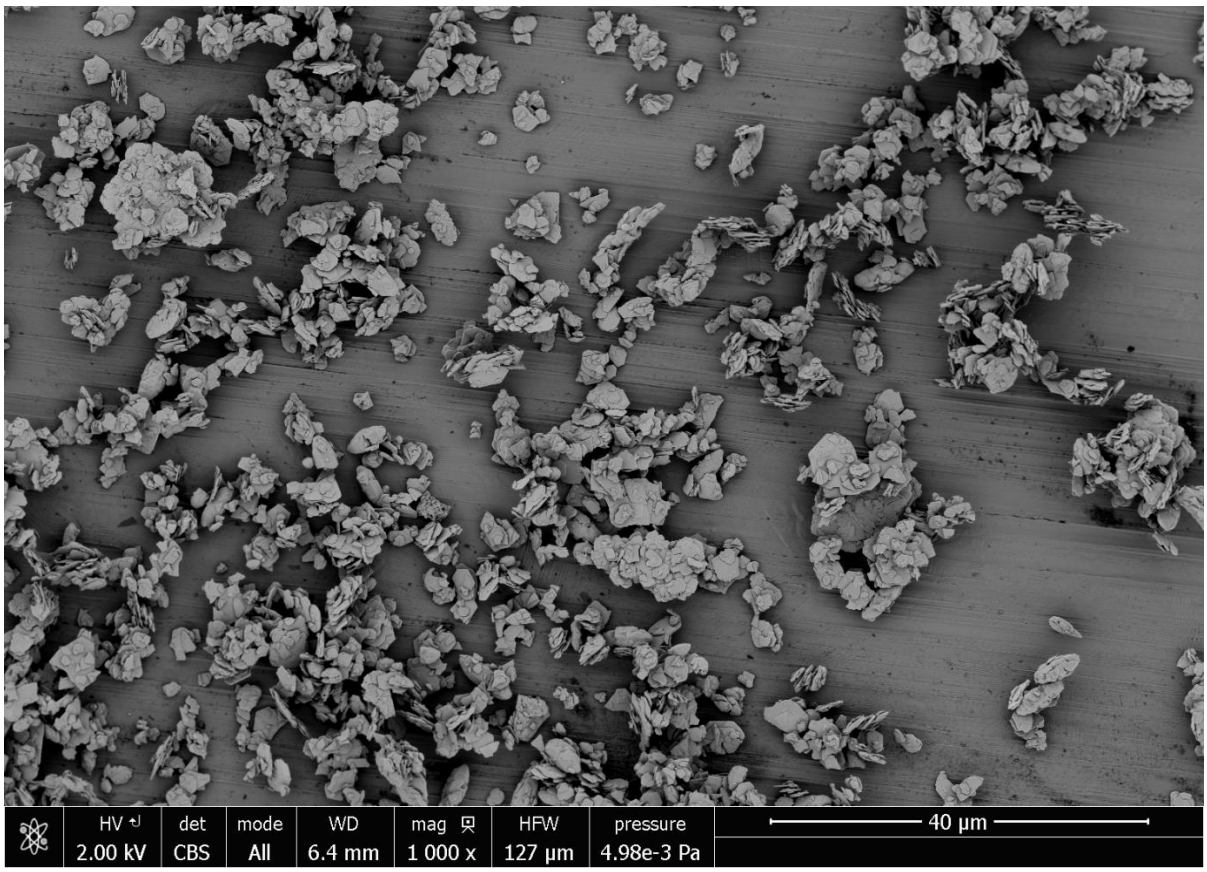


Figure 17. FEG-SEM image in CBS mode showing Lead White Schoonhoven (1000 x magnification). Image acquired by Ineke Joosten.

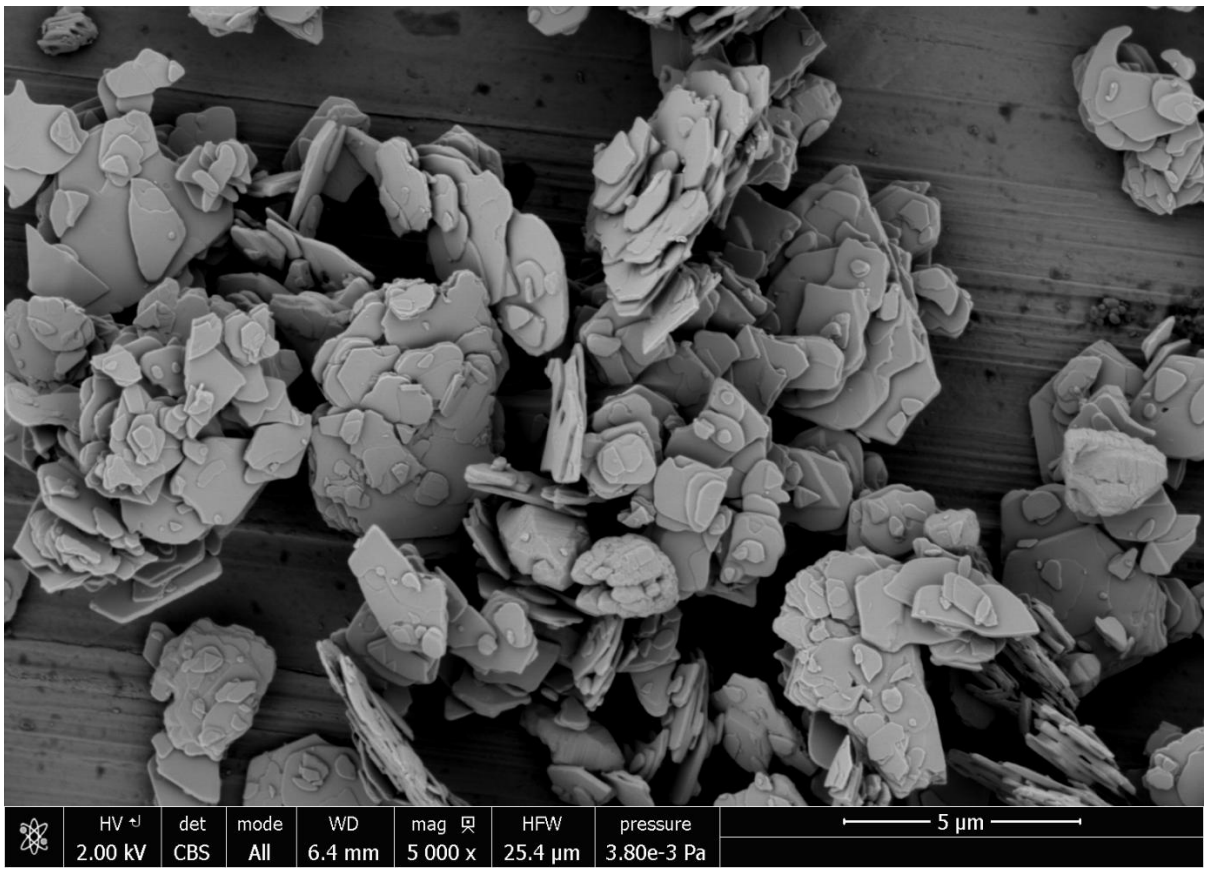


Figure 18. FEG-SEM image in CBS mode showing Lead White Schoonhoven (5.000 x magnification). Image acquired by Ineke Joosten.

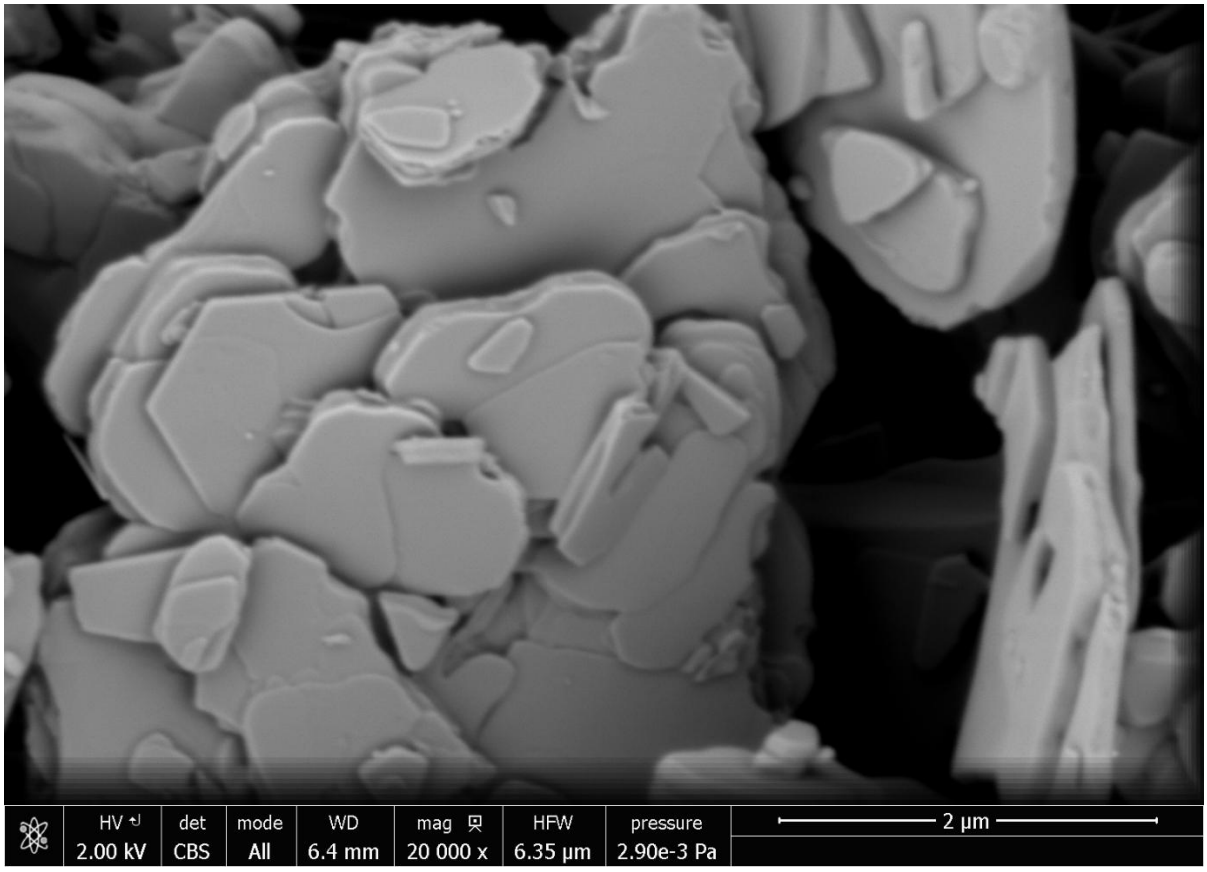
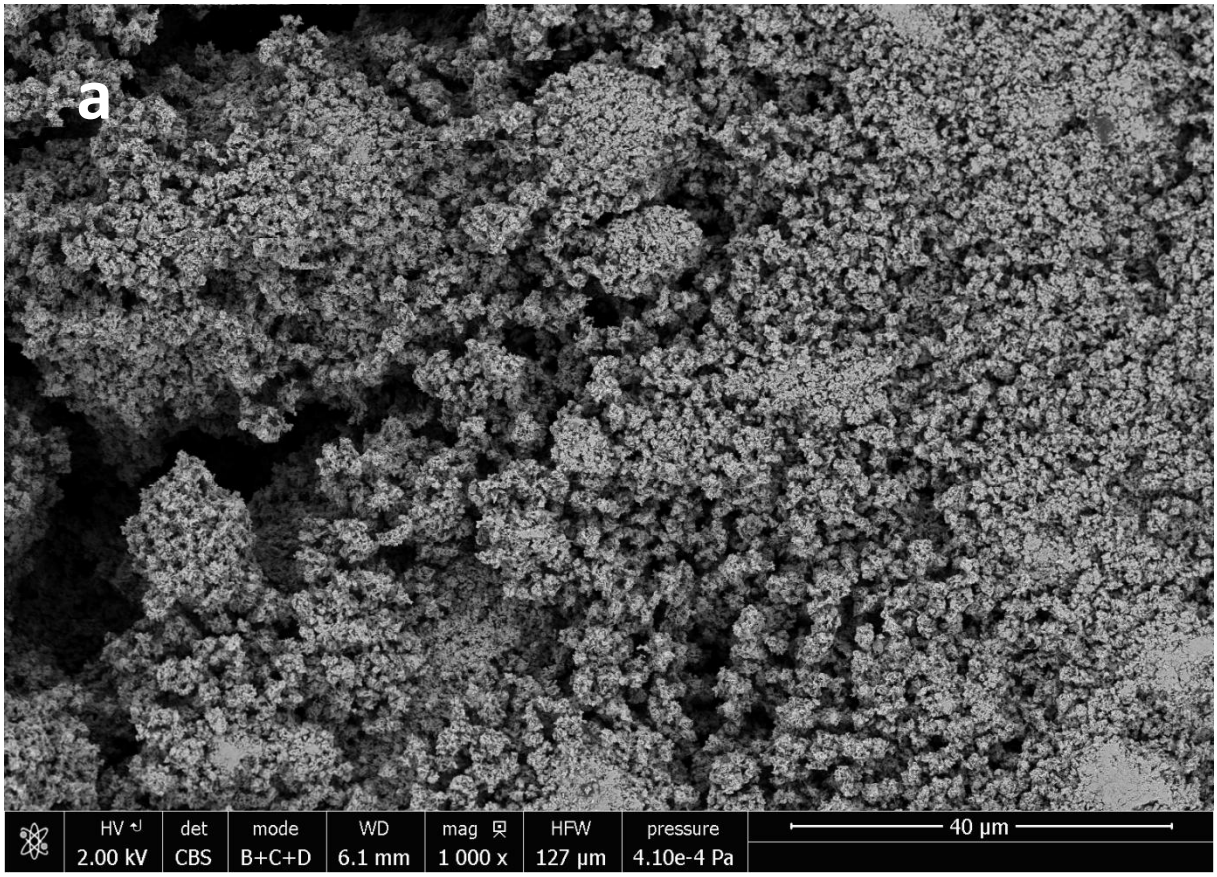


Figure 19. FEG-SEM image in CBS mode showing Lead White Schoonhoven (20.000 x magnification). Image acquired by Ineke Joosten.

4.2. FEG-SEM Images of Zinc White pigments



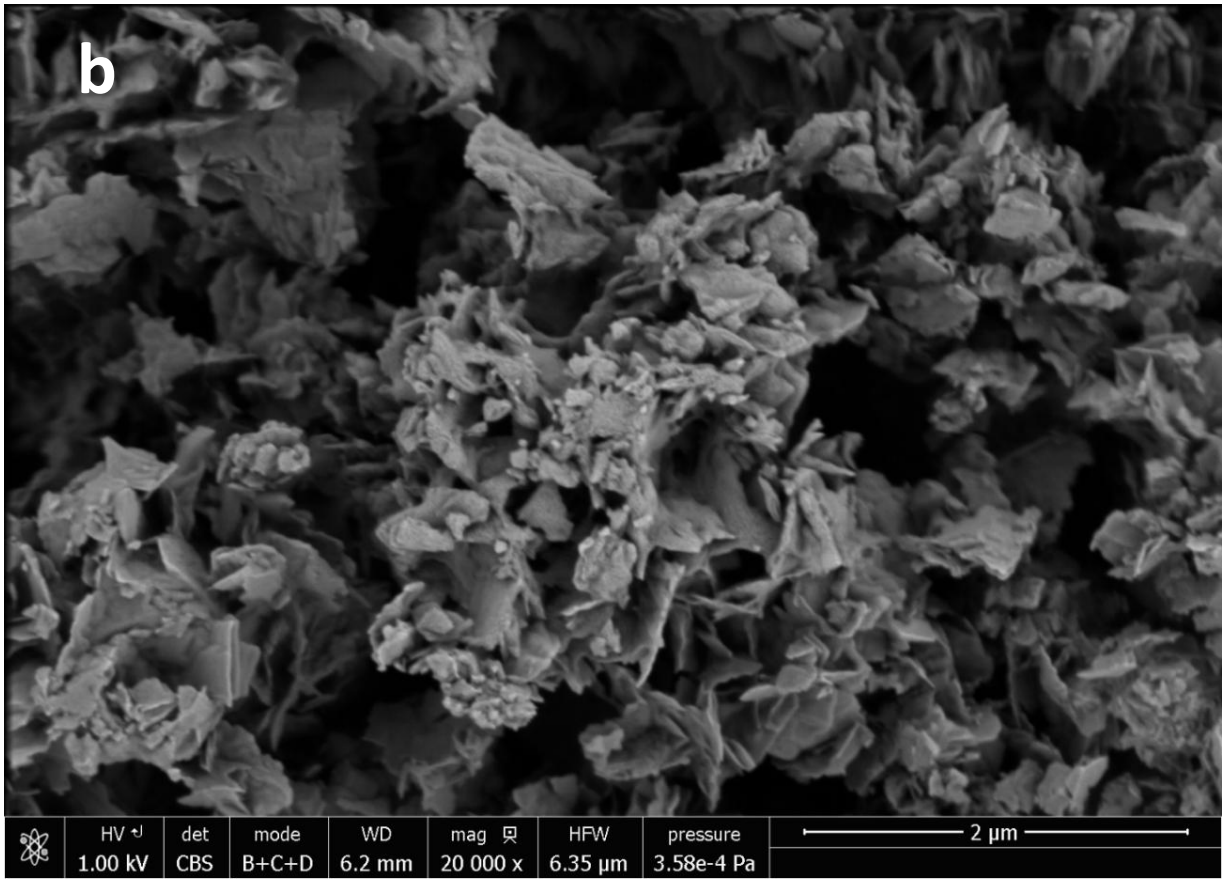


Figure 20. FEG-SEM images in CBS mode showing Zinc White 9647 at a) 1.000 x, and b) 20.000 x magnification. Image acquired by Ineke Joosten.

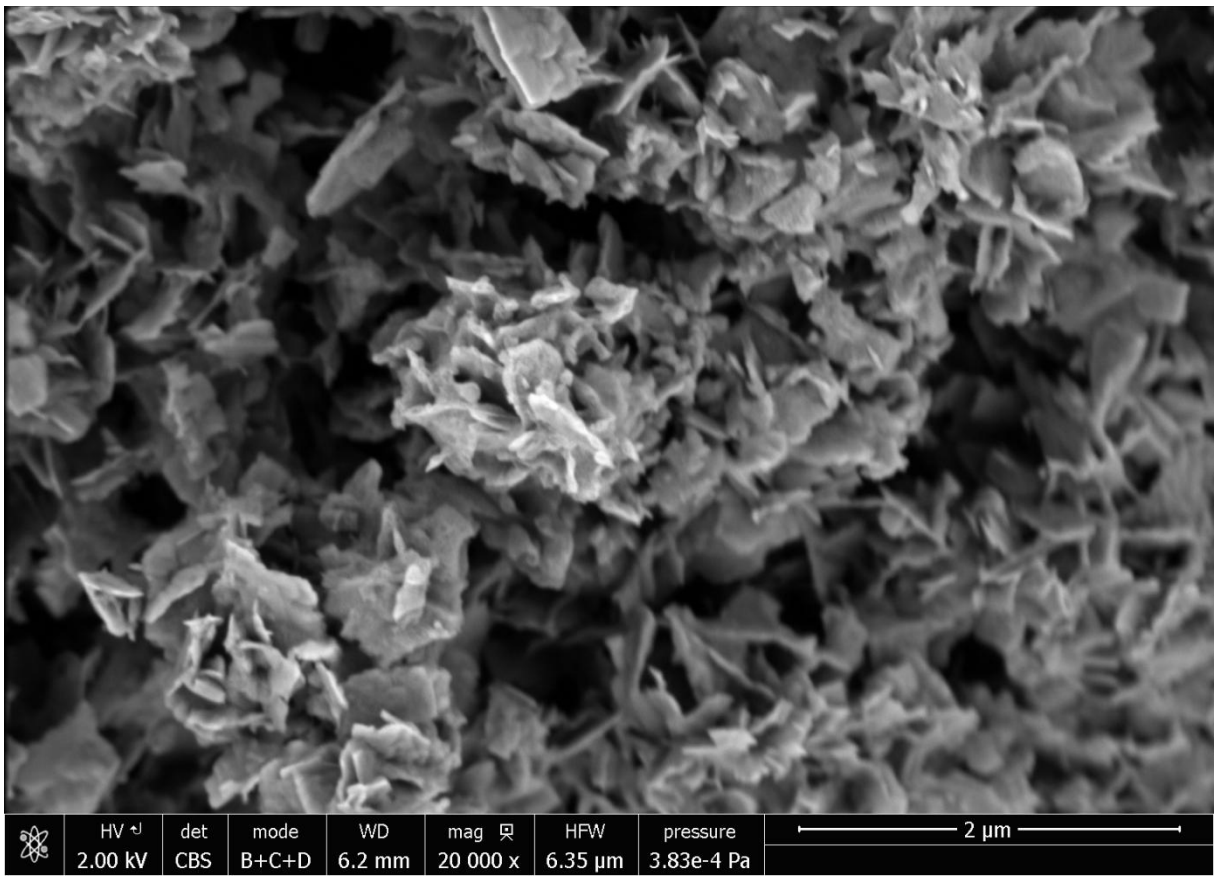


Figure 21. FEG-SEM image in CBS mode showing Zinc White 9647 (20.000 x magnification). Image acquired by Ineke Joosten.

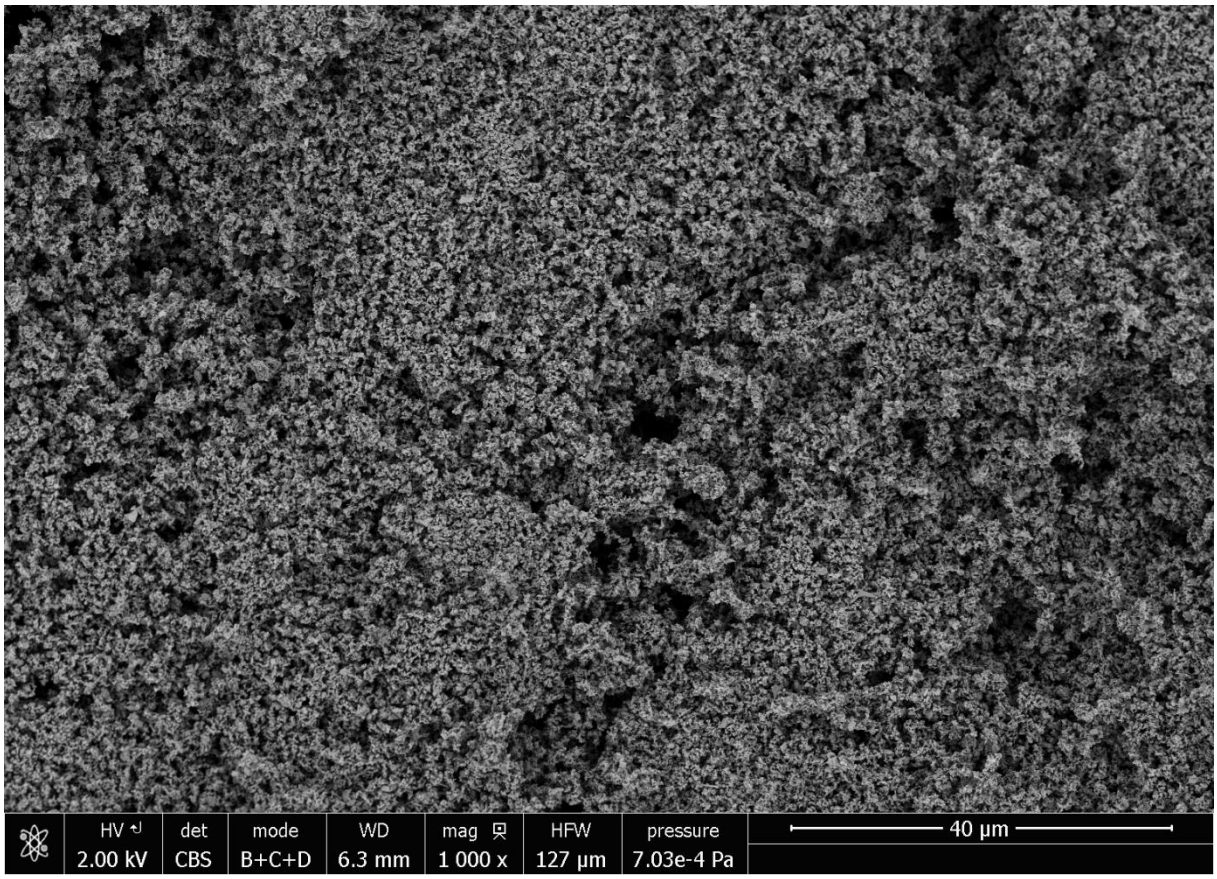


Figure 22. FEG-SEM image in CBS mode showing Zinc White Carlyle (1.000 x magnification). Image acquired by Ineke Joosten.

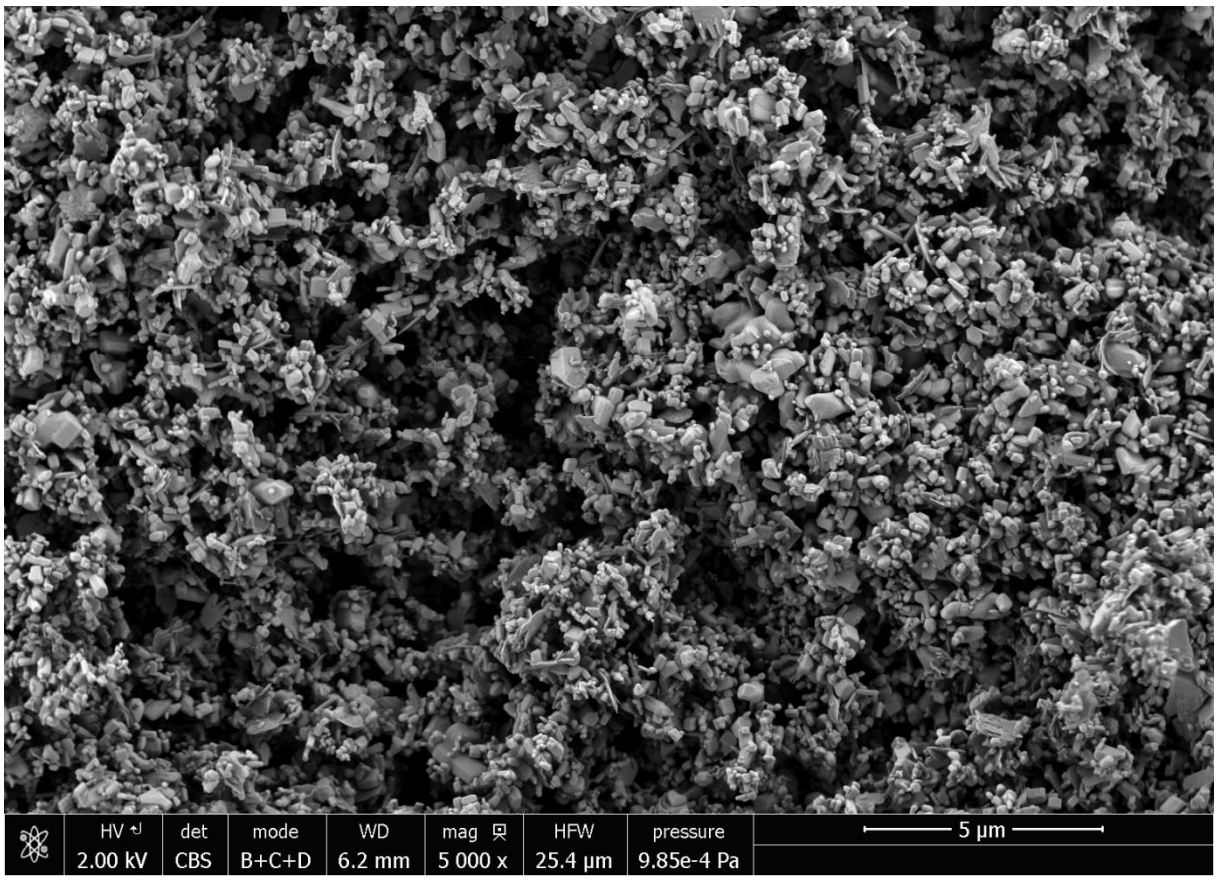


Figure 23. FEG-SEM images in CBS mode showing Zinc White Carlyle (5.000 x magnification). Image acquired by Ineke Joosten.

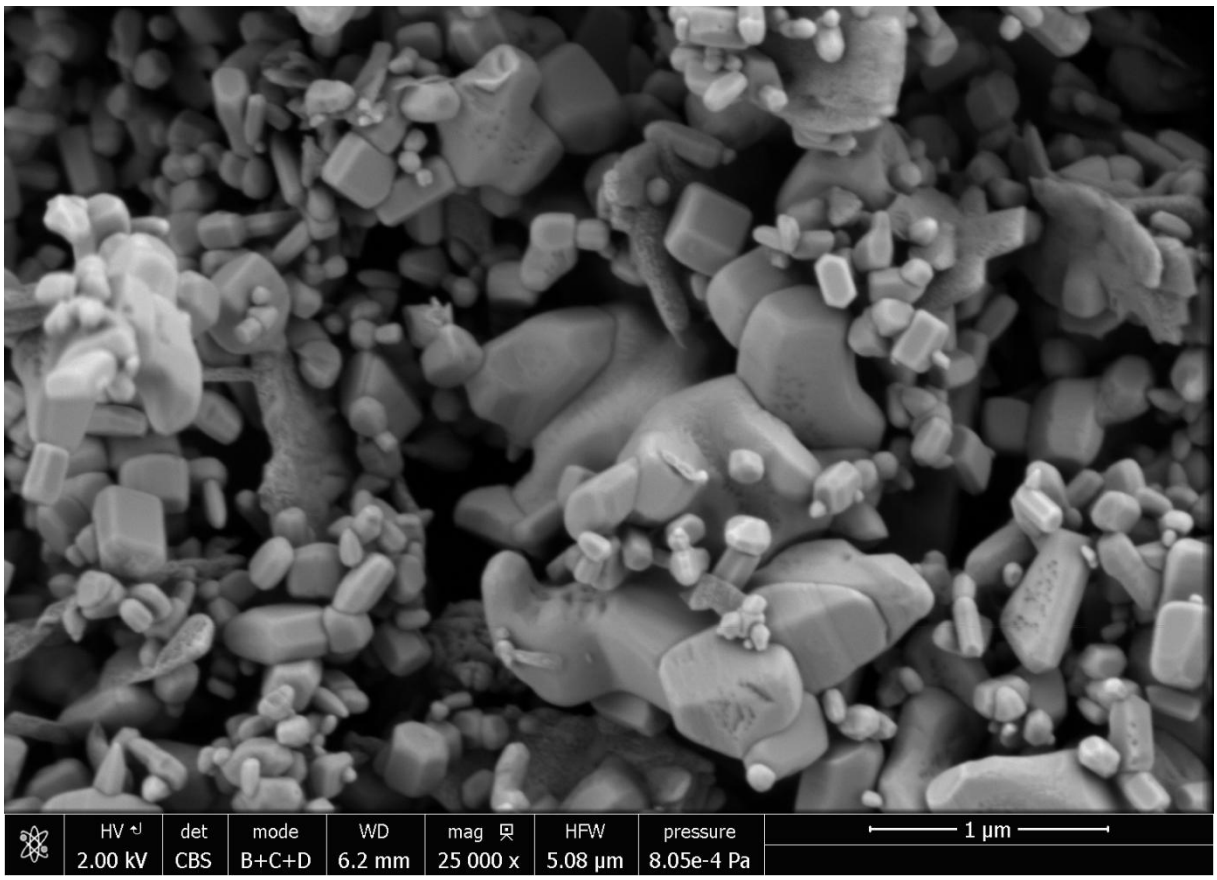


Figure 24. FEG-SEM image in CBS mode showing Zinc White Carlyle (25.000 x magnification). Image acquired by Ineke Joosten.

4.2. FEG-SEM Images of Titanium White Pigments

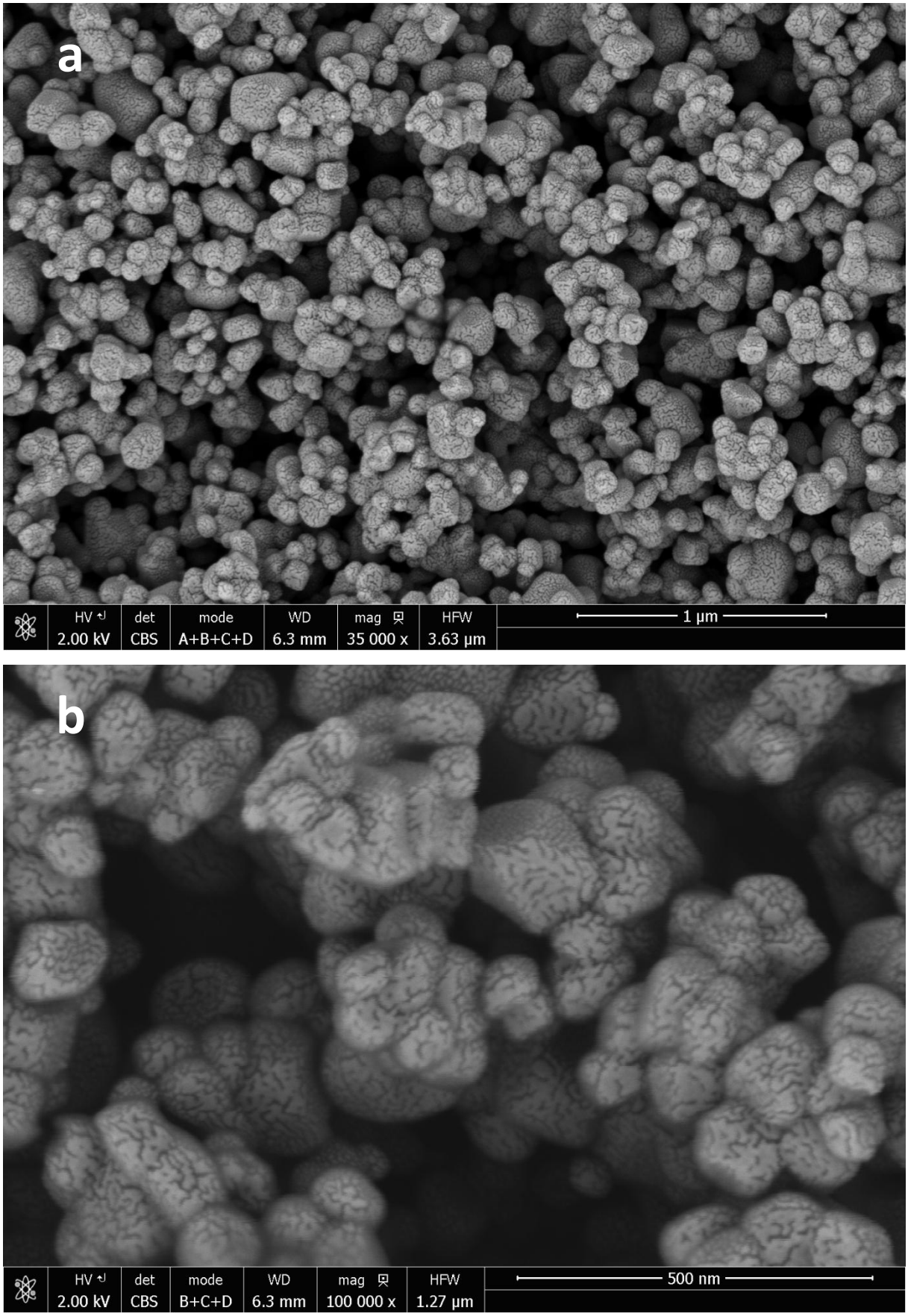


Figure 25. FEG-SEM images in CBS mode showing gold coated A3 at a) 35.000 x, and b) 100.000 x magnification. Image acquired by Ineke Joosten.

5.1. Selected (S)TEM-EDX Phase-maps and spectral images of Lead White Pigments

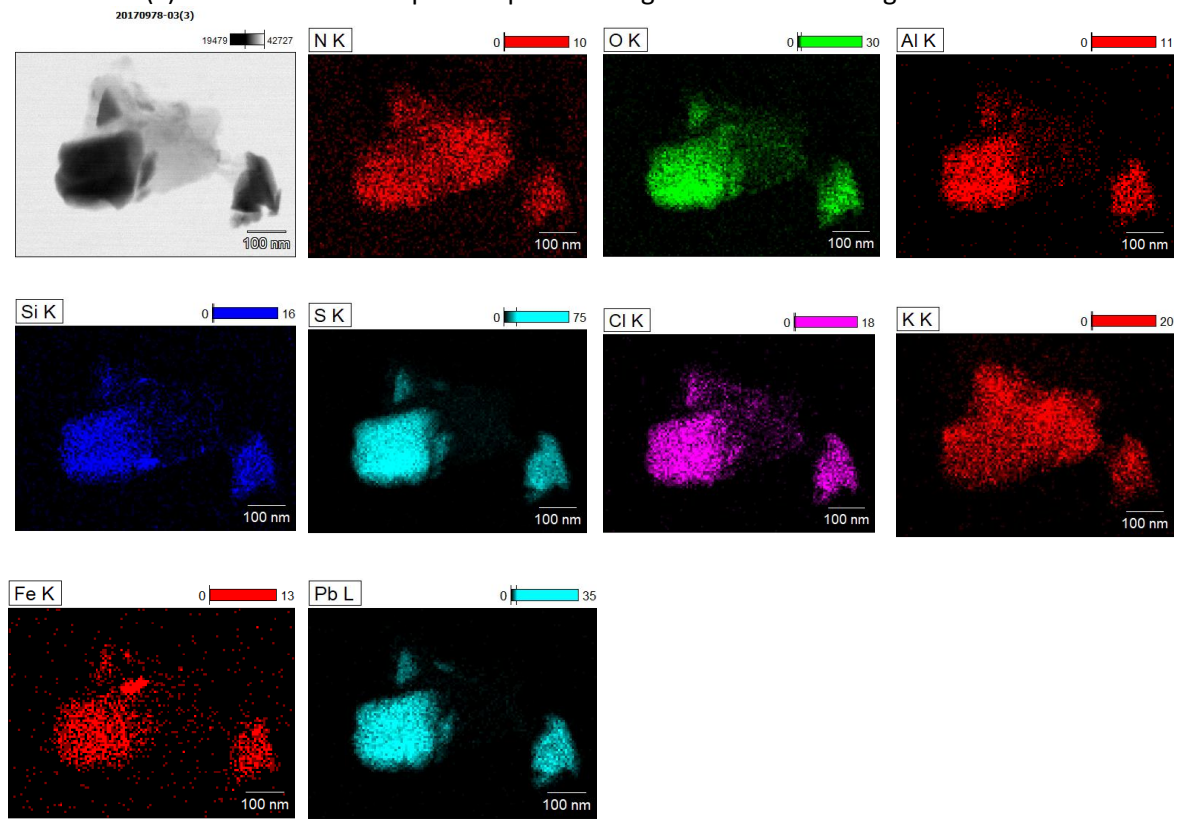
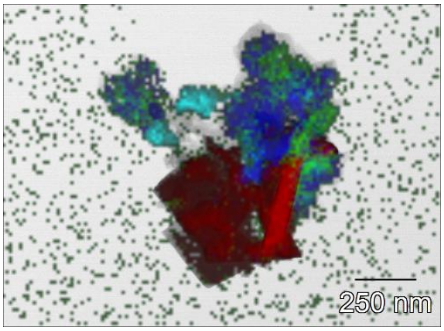


Figure 26. (S)TEM-EDX phase maps of Schoonhoven Lead White pigment, from the Carlyle MOLART fellowship, analysis and results were provided by AKZO NOBEL Chemicals.



Phase 1: Pb Carbonate

Phase 2: Carbon Support

Phase 3: Silicate

Phase 4: Ca Carbonate

Element	Phase 1	±	Phase 2	±	*Phase 3	±	*Phase 4	±
C	19.4	0.4	91.0	0.6	47.3	0.7	40.1	1.2
N	1.7	0.2	n.d.	n.d.	2.2	0.5	n.d.	n.d.
O	7.8	0.1	3.6	0.1	15.8	0.3	28.3	0.6
Al	0.3	<0.1	0.2	<0.1	1.6	0.1	0.9	0.1
Na	n.d.	n.d.	0.3	<0.1	1.2	0.1	0.8	0.3
Mg	n.d.	n.d.	1.4	<0.1	0.4	<0.1	0.8	0.1
Si	n.d.	n.d.	n.d.	n.d.	13.7	0.2	n.d.	n.d.
P	n.d.	n.d.	n.d.	n.d.	0.3	<0.1	n.d.	n.d.
S	n.d.	n.d.	0.3	<0.1	2.2	0.1	3.4	0.2
Cl	0.9	0.1	0.2	<0.1	0.8	0.1	0.6	0.1
K	0.2	<0.1	0.2	<0.1	1.0	0.1	0.6	0.1
Ca	0.4	0.1	0.3	<0.1	1.6	<0.1	23.9	0.5
Ti	0.2	<0.1	n.d.	n.d.	0.4	<0.1	n.d.	n.d.
Fe	0.2	<0.1	0.1	<0.1	1.0	0.1	n.d.	n.d.
Pb	69.0	0.97	2.5	0.2	10.2	0.4	n.d.	n.d.

• c

Figure 27. (S)TEM-EDX phase-map results of Lead White sample, Kremer Pigmente©, from the Carlyle MOLART fellowship, analysis and results were provided by AKZO NOBEL Chemicals.

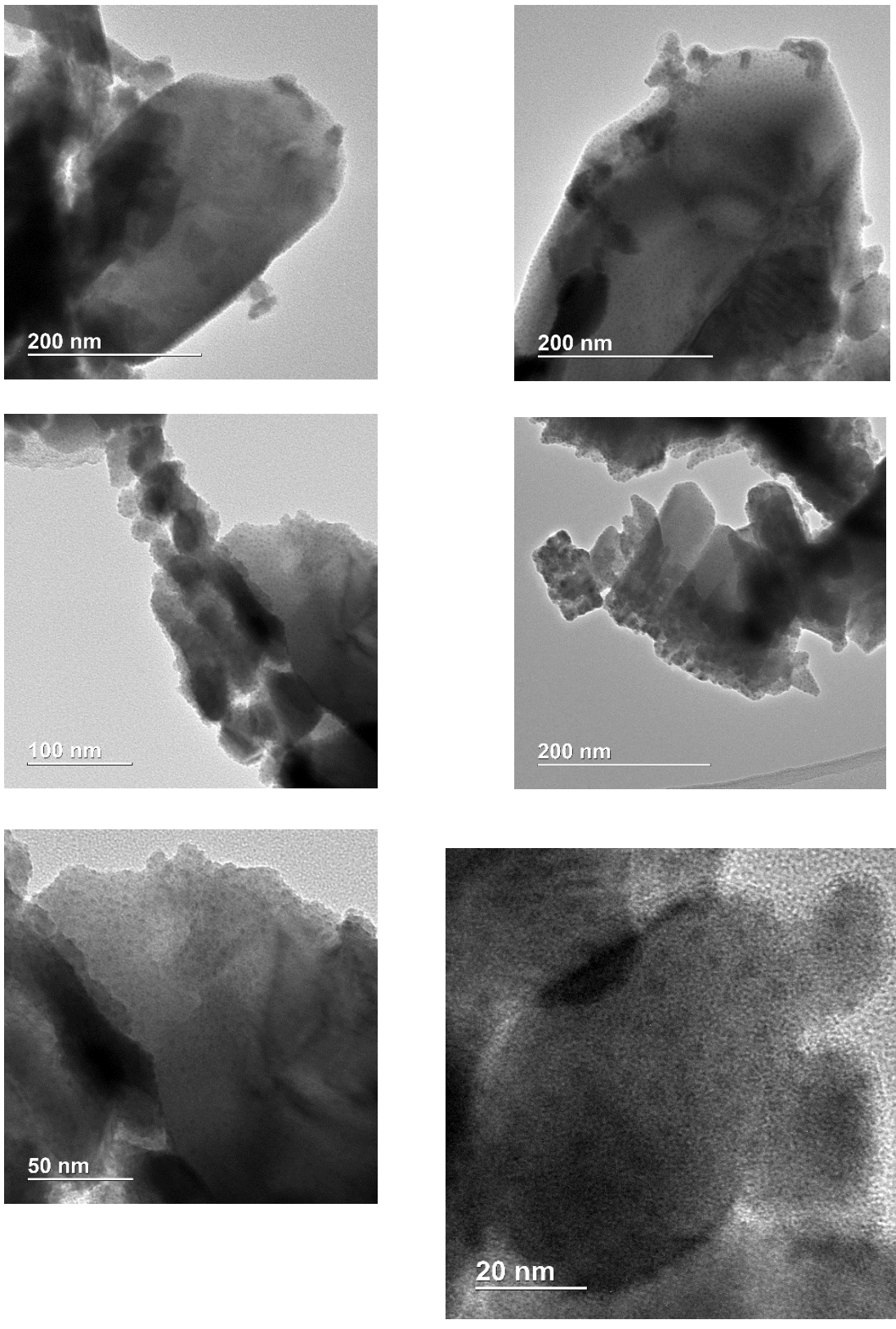
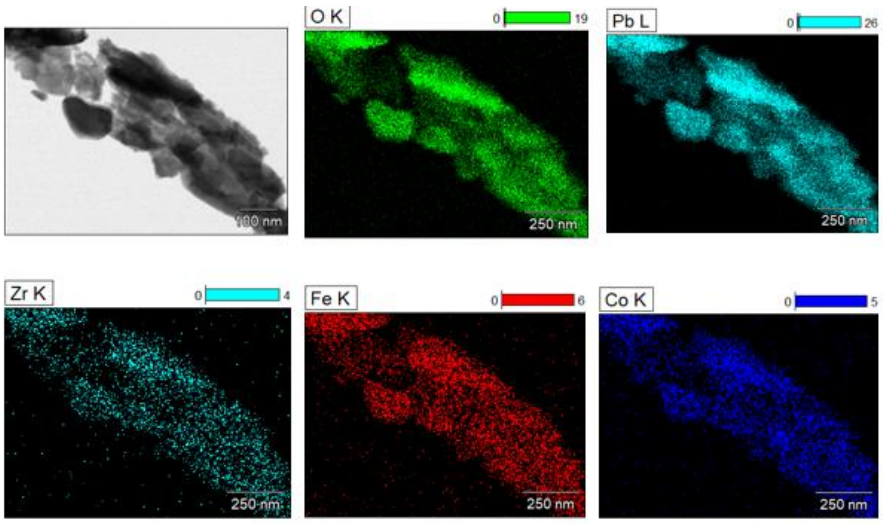


Figure 28. (S)TEM-EDX spectral images of 8233 Lead White pigment, from the RCE reference pigment collection. Analysis and results were provided by AKZO NOBEL Chemicals.



Element	SI-01	±
C	22.1	0.3
O	8.3	0.3
Fe	0.2	<0.1
Co	0.3	<0.1
Zr	1.5	0.2
Pb	67.7	0.5

Figure 29. (S)TEM-EDX spectrla image and phase maps of 8233 Lead White pigment, from the RCE reference pigment collection. Analysis and results were provided by AKZO NOBEL Chemicals.

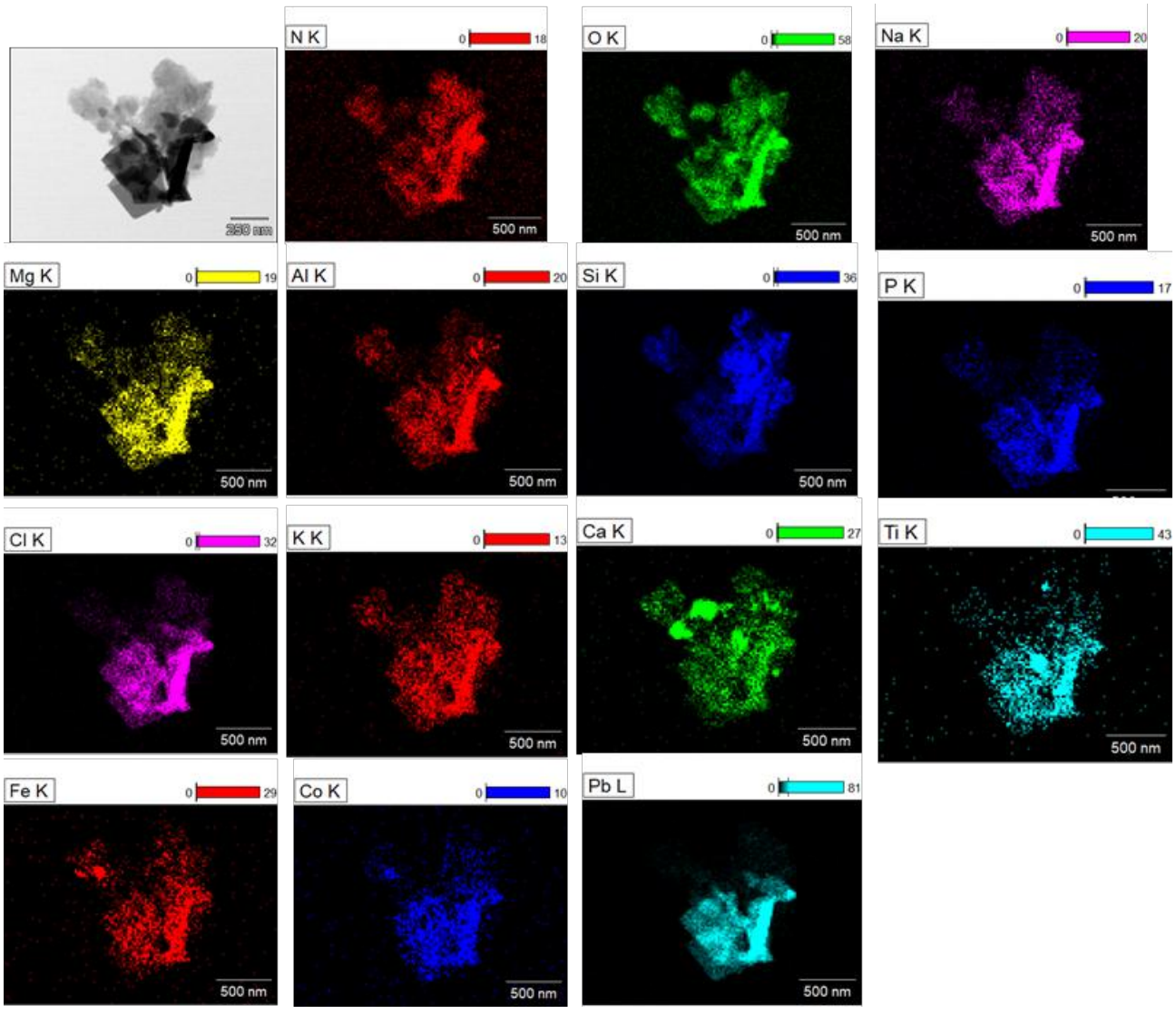
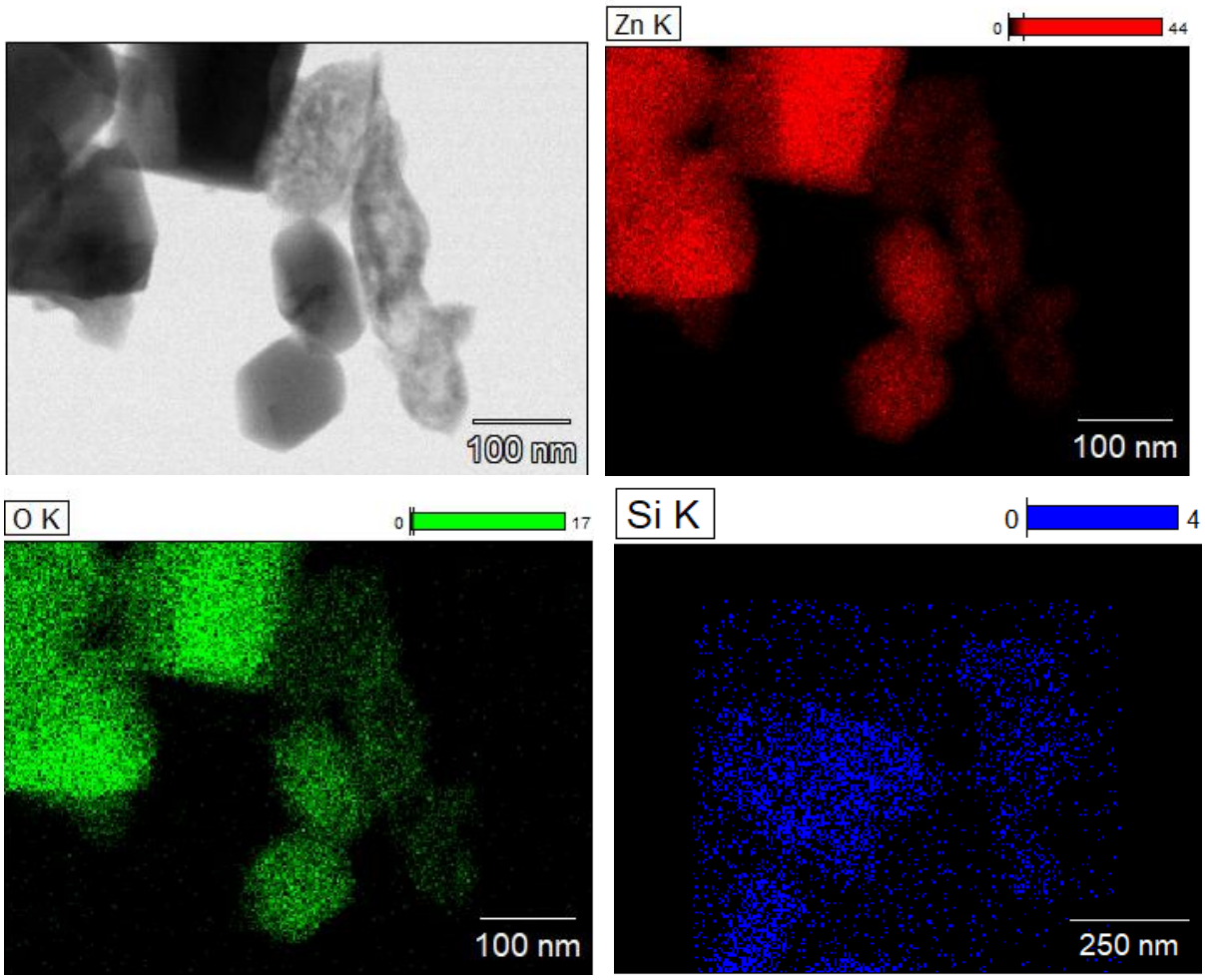


Figure 30. (S)TEM-EDX spectral image and phase maps of Kremer Pigmente Lead White pigment, from the RCE reference pigment collection. Analysis and results were provided by AKZO NOBEL Chemicals.

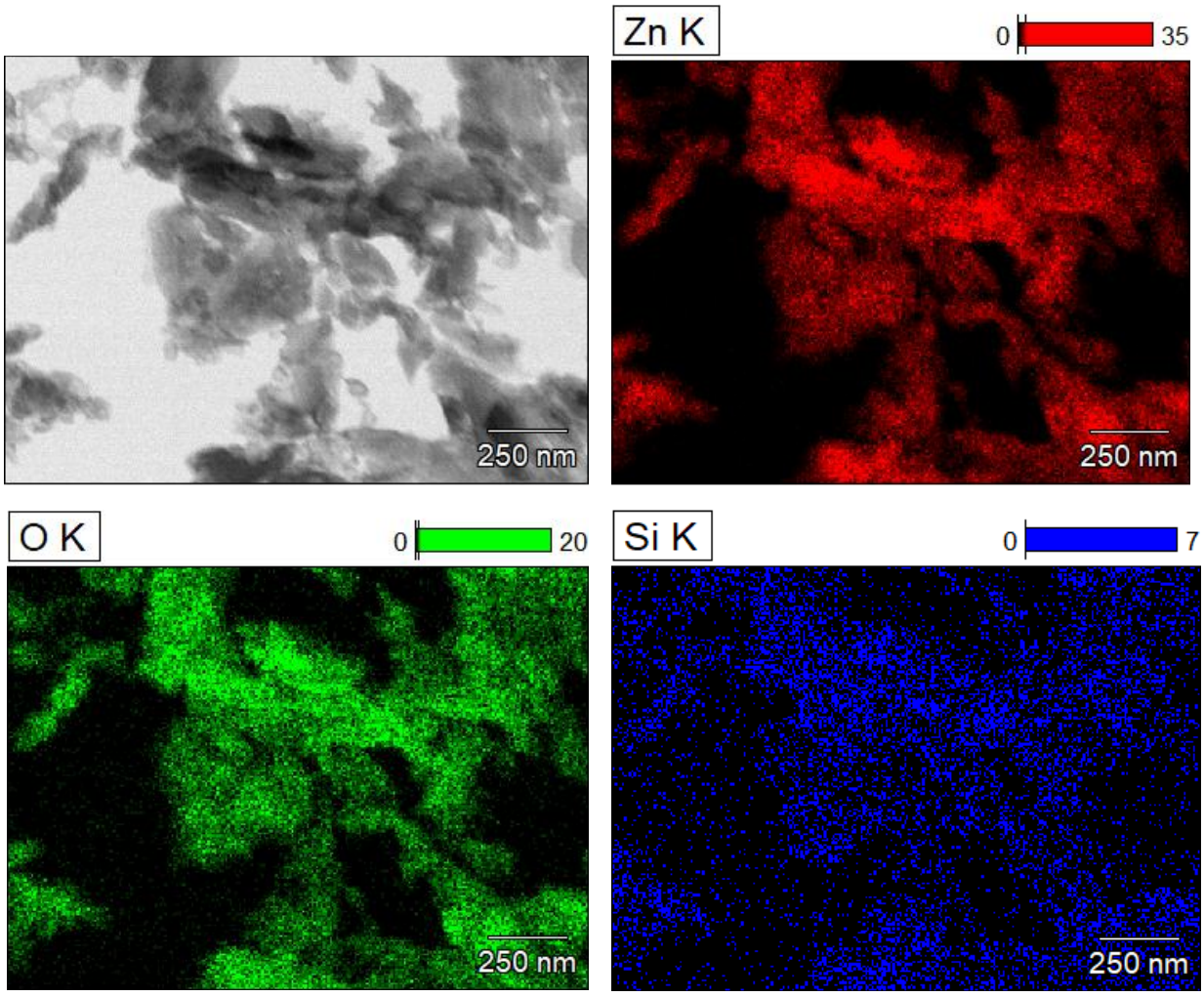
5.2. Selected (S)TEM-EDX Phase-maps and spectral images of Zinc White Pigments



Element	Wt.%	±
O	18.3	0.1
Si	0.4	<0.1
Zn	81.3	0.3

* Si may derives from contamination

Figure 31. (S)TEM-EDX phase maps of Zinc White 0191 from the RCE reference pigment collection. Analysis and results were provided by AKZO NOBEL Chemicals.



Element	Wt.%	±
O	29.2	0.4
*Si	1.7	<0.1
Zn	69.1	0.3

*Si may derived from contamination

Figure 32. (S)TEM-EDX phase maps of Zinc White 9647 from the RCE reference pigment collection. Analysis and results were provided by AKZO NOBEL Chemicals.

5.3. Selected (S)TEM-EDX Phase-maps and spectral images of Titanium White Pigments

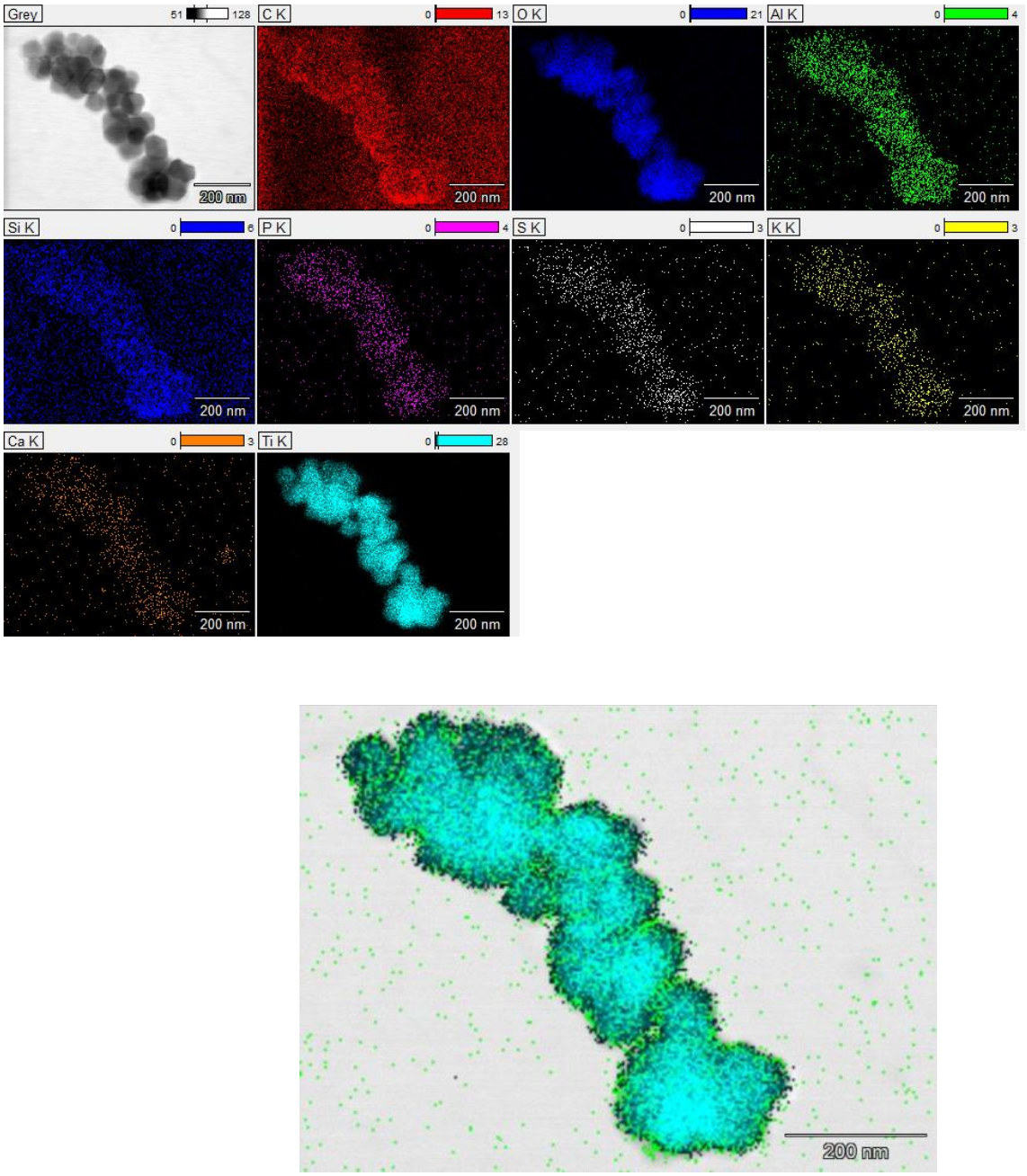
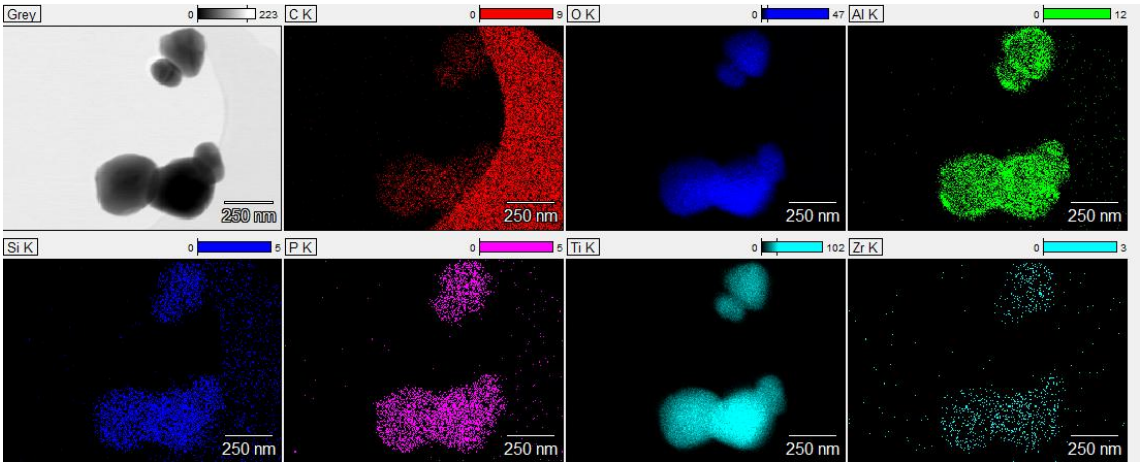
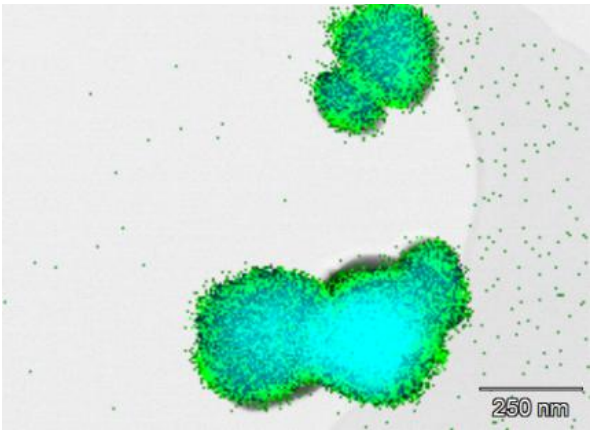
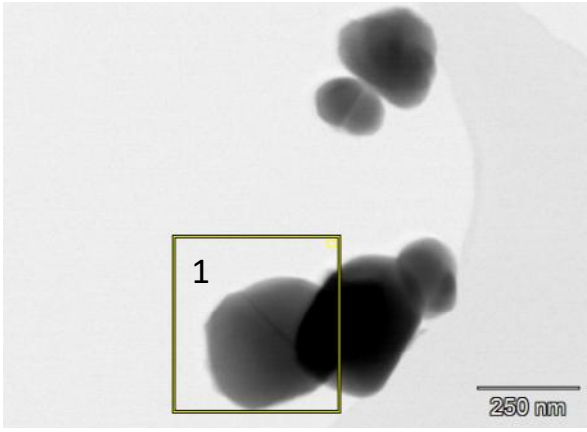


Figure 33. (S)TEM-EDX image mapping of A3. Both Al and Si are present in the coating on the TiO_2. In addition, P, S, K and Ca are present in very low amounts, and all evenly distributed over the pigment. These results are from AKZO NOBEL Chemicals.







Atom Conc%

	C	O	Al	Si	P	Ti	Zr
stem2d-1	4.5	52.4	1.5	0.2		41.2	0.3

Figure 29. (S)TEM-EDX image mapping of R3. Both Al and Zr are present in the coating on the TiO_2. These results are from AKZO NOBEL Chemicals.

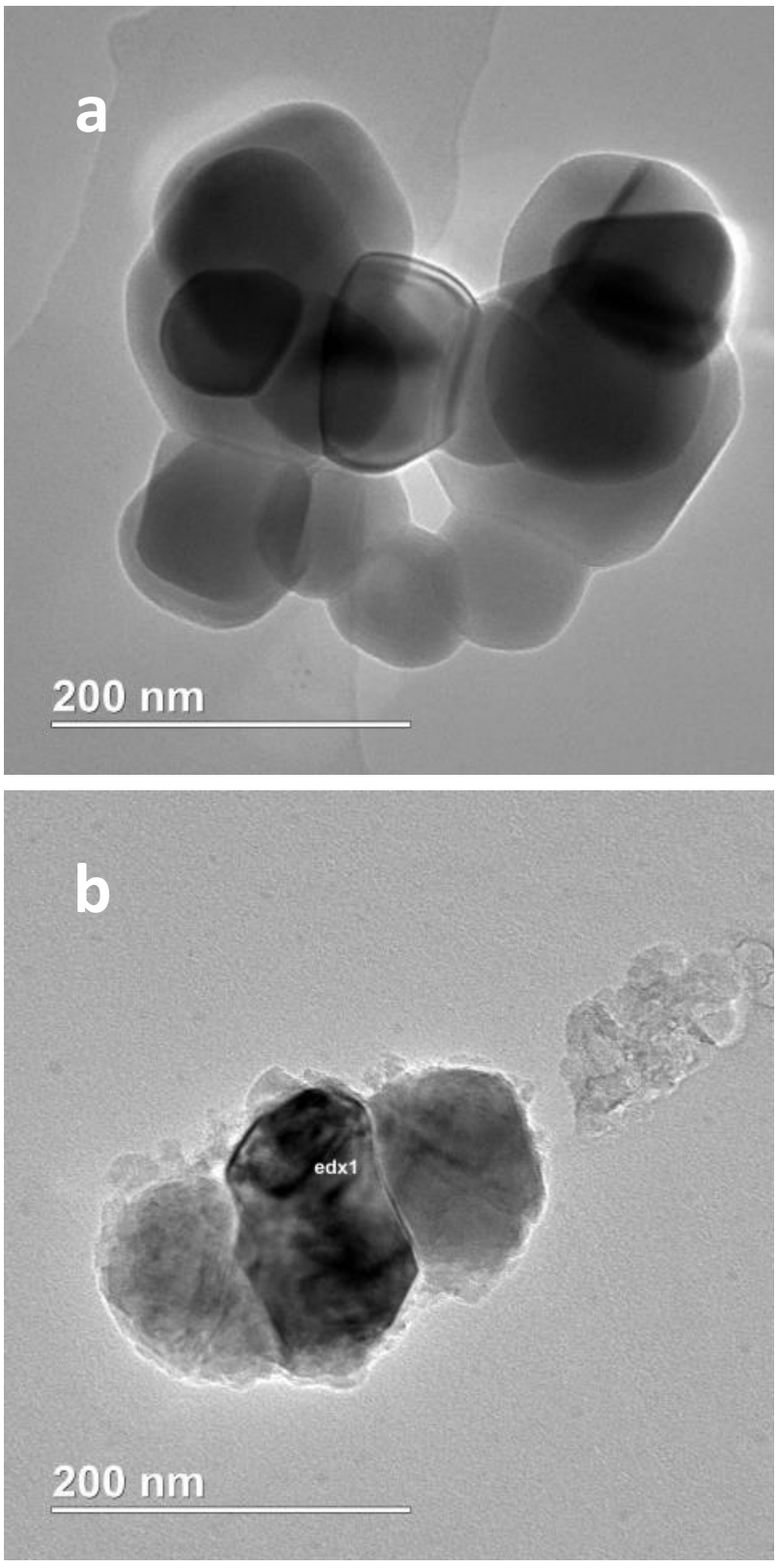


Figure 30. (S)TEM-EDX spectral image of A2 (a), above, where there is no visible evidence of an inorganic coating, and, below, spectral image of A3 (b) where coating material is visible. The material surrounding the particles is inhomogeneous and loose coating material can be observed. Results from AKZO NOBEL Chemicals.

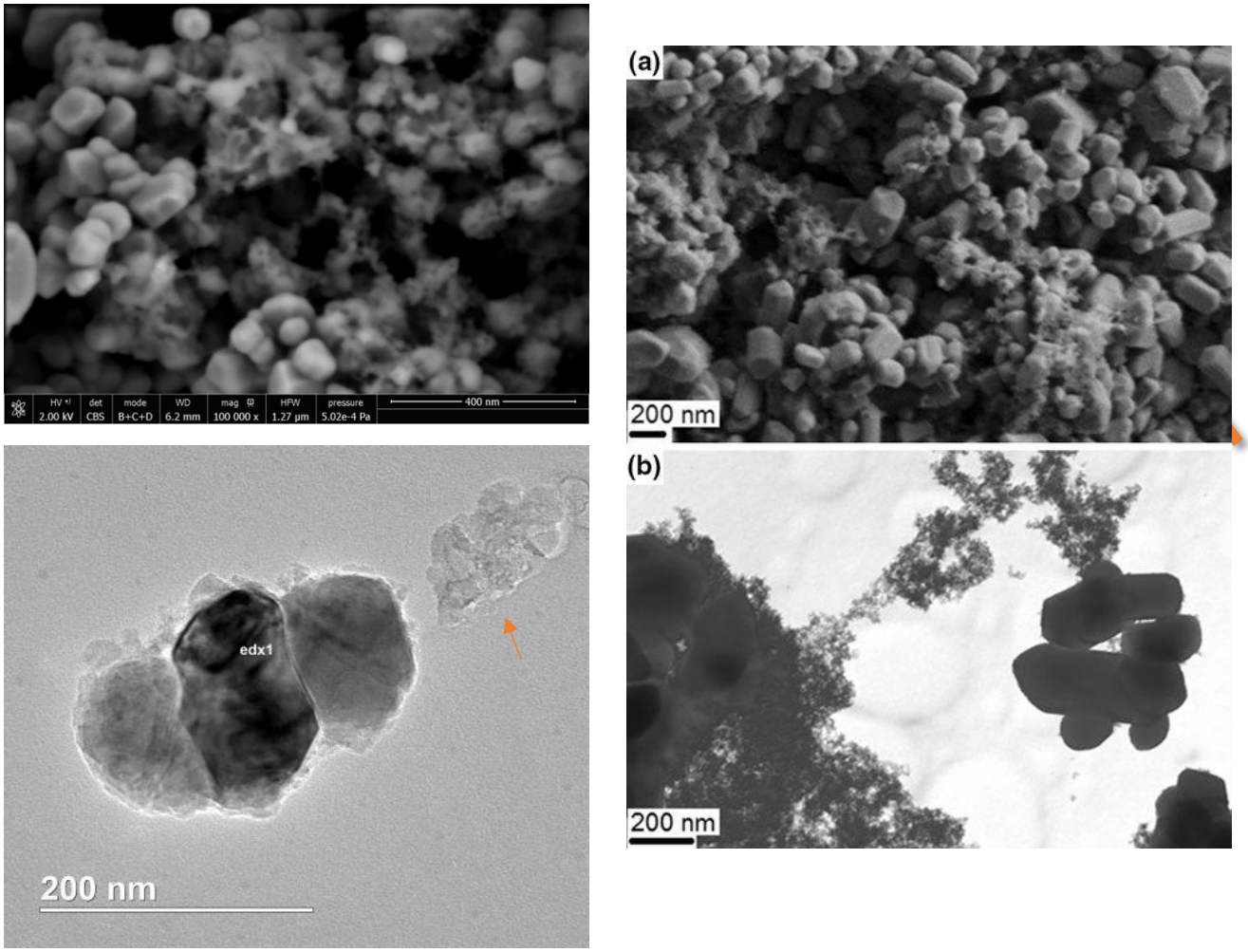


Figure 31.On the top left, a FEG-SEM image in CBS mode of A3 (100.000 x magnification) shows a distinct morphology, a kind of powdery material on top of the particles which may belong to the loose coating material is visible with the TEM-BF (lower left corner). On the right, an example of an unsuccessful coating fom the literature (taken at magnification of 80 x 10^3 and 150 x 10^3, respectively), which appears very similar [Image taken from (Veronovski and Verhovsek 2014) [46]].